Department of Chemistry
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$\delta^{13}C$ and δD measurements of volatile organic compounds in a variety of emissions by thermal desorption compound specific isotope analysis

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Doctor of Philosophy
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DECLARATION

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgement has been made.

This thesis contains no material that has been accepted for the award of any other degree or diploma in any university.

Christiane D. Vitzthum von Eckstaedt

Perth, February 14, 2011

To my husband

who holds my heart and my soul

ABSTRACT

Volatile organic compounds (VOCs) can be related to different compound classes but they all have a distinct vapour pressure allowing them to enter the atmosphere under ambient conditions. VOCs can undergo various reactions in the atmosphere and are emitted by various processes (anthropogenic and natural). Compound specific isotope analysis (CSIA) has been used in many other research studies to track the fate and source of compounds in the environment and the geological record. The majority of CSIA has been applied to extracts from soil, sediment or crude oils requiring entirely different sampling techniques compared to atmospheric samples. Applying CSIA to atmospheric compounds is a growing research field but has mainly being restricted to stable isotopes of carbon.

This PhD thesis presents a novel application for adsorptive sampling on TenaxTA to analyse compound specific $\delta^{13}C$ and δD of a range of atmospheric VOCs (C_6 - C_{10}). For the first time a 2-stage thermal desorption (TD) unit was linked to gas chromatography isotope ratio mass spectrometry (GC-irMS) and instrumental conditions were thoroughly investigated and optimised. Results obtained by using a standard mix of eleven VOCs confirmed reliability of TD-GC-irMS analyses with standard deviations (SD) below instrument precision. δ values showed negligible isotopic fractionation compared to results obtained from traditional GC-irMS analysis (without TD unit) demonstrating the suitability of TD for CSIA.

The technique was applied to analyse VOCs from various emission sources, e.g. car exhaust, biomass combustion and an industry stack. The results obtained have provided some insight into the formation processes of the VOCs investigated. $\delta^{13}C$ values from an alumina refinery emission support a natural origin for the VOCs (organic material in bauxite ore). The δD values (21 to -137 ‰) of the industry emission were consistently more enriched in D compared to δD values of VOCs previously reported making the δ values of

VOCs in the industrial stack unique. Car exhaust emission from a petrol engine showed significant differences in δ values for VOCs up to 2 ‰ and 25 ‰ ($\delta^{13}C$ and δD, respectively) at different tank fuel levels when using the same fuel batch. Car exhaust emission samples from a diesel engine showed a high content of highly complex mixture of unresolved compounds thus chromatographic baseline separation of VOCs was not achieved for stable hydrogen isotope analysis and led to unreliable δ values. The results from different biomass combustion emissions (including 5 species of C3 plants and 3 species of C4 plants) confirmed significant differences in $\delta^{13}C$ of VOCs between C3 and C4 plants due to their specific metabolic pathways for carbon fixation in photosynthesis. The δD of VOCs derived from dicotyledons were less depleted in D compared to δD of VOCs derived from grasses (differences >27 ‰) indicating that the VOCs are derived mainly from lignin/cellulose rather than from lipids since dicotyledons contain higher amounts of lignin/cellulose.

Due to the unique isotopic signatures of the VOCs from the different emission sources it was possible to distinguish their origins. Furthermore, TD-GC-irMS shows great potential to establish other emission sources in the environment and may help to gain some insight into their modes of formation.

ACKNOWLEDGMENTS

Firstly I would like to express my gratitude to my principle supervisor, Prof. Kliti Grice, for her advice and scientific input and guidance during my PhD study and for never failing to demonstrate to have faith in me. Thanks to Kliti I have had the opportunities to attend and present this research at national and international conferences. I gained enormously from her remarkable writing skills and feedback on publications. I always felt supported when challenged.

I wish to thank my associate supervisor Dr. Marisa Ioppolo-Armanios for support and helpful discussions. I thank Mark Jones for technical advice, climbing up industry stacks to take samples and for introducing me to challenging rebus puzzles. I would like to thank both for their valuable feedback on my papers.

Thanks also to Geoff Chidlow for persistent help on all instrumental issues and for always, magically, having a spare part at the ready. Thanks also to Sue Wang, Stephen Clayton and Svenja Tulipani for valuable discussions on isotope analysis. I also thank David Kelly for his effort in providing all the necessary equipment for the biomass combustion experiments. Further, I would like to thank Delia Giggins for sorting out various scholarship intricacies and Tanya Chambers for solving all sorts of administrative problems and making things possible. Thanks to my PhD colleagues in the WA Organic and Isotope Geochemistry Centre who enriched not only my scientific but my cultural knowledge, particularly Birgit Nabbefeld, Ercin Maslen and Dawn White who carried me through this tough time and rewarding me with a life time friendship.

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Very special thanks to my family for their unwavering support across continents and oceans, for providing everything I needed to get this far and for surrendering my company so that I can realise my goals. Many thanks go to Erika and Roland Hähnel for the various escapes to their farm to recharge my energy and for giving me the feeling of family whilst being far away from my own.

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Christiane D. Vitzthum von Eckstaedt
Perth, February 14, 2011

PRIMARY PUBLICATIONS

This thesis is assembled by publications, either in press, in review or to be submitted, which form the individual chapters and are listed below.

CHAPTER 2

Vitzthum von Eckstaedt, C.; Grice, K.; Ioppolo-Armanios, M.; Jones, M.; Chidlow, G. δD and $\delta^{13}C$ analyses of atmospheric volatile organic compounds by thermal desorption gas chromatography isotope ratio mass spectrometry. *Journal of Chromatography A*, 1218 (2011), 6511–6517. Excellence Research Australia (ERA) A* rated publication.

CHAPTER 3

Vitzthum von Eckstaedt, C.; Grice, K.; Ioppolo-Armanios, M.; Jones, M. $\delta^{13}C$ and δD of volatile organic compounds in an alumina industry stack emission. *Atmospheric Environment,* 45 (2011), 5477-5483. Excellence Research Australia (ERA) A rated publication.

CHAPTER 3

Vitzthum von Eckstaedt, C.; Grice, K.; Ioppolo-Armanios, M.; Kelly, D.; Gibberd, M. Compound specific $\delta^{13}C$ and δD analyses of volatile organic compounds in various emissions. *Chemosphere*, submitted (2011). Excellence Research Australia (ERA) A rated publication.

CONTRIBUTIONS OF OTHERS

The work presented in this thesis was primarily designed, experimentally executed, interpreted, and the individual manuscripts were prepared by the first author (Christiane D. Vitzthum von Eckstaedt). Contributions by co-authors are described below.

CHAPTER 2

Christiane D. Vitzthum von Eckstaedt and Geoff Chidlow worked on the set up of the instrumental hardware, especially connecting the thermal desorption unit to gas chromatography instruments and participated in instrumental trouble shooting. Instrumental maintenance, method development, sampling, isotope analysis and data processing were performed by Christiane D. Vitzthum von Eckstaedt with assistance from Kliti Grice. Initial sampling tests were carried out by Christiane D. Vitzthum von Eckstaedt and Mark Jones. Christiane D. Vitzthum von Eckstaedt and Kliti Grice interpreted results. Christiane D. Vitzthum von Eckstaedt led the paper, Kliti Grice, Marisa Ioppolo-Armanios and Mark Jones contributed to the writing of the paper.

CHAPTER 3

Christiane D. Vitzthum von Eckstaedt and Mark Jones developed the set up for multi-tube sampling and carried out the industry stack emission sampling at Alcoa's refinery site. Isotope and compound identification analyses were performed by Christiane D. Vitzthum von Eckstaedt. Christiane D. Vitzthum von Eckstaedt, Kliti Grice, Marisa Ioppolo-Armanios interpreted results, and Christiane D. Vitzthum von Eckstaedt wrote the paper. Kliti Grice, Marisa Ioppolo-Armanios provided intellectual input through discussions on the results. Kliti Grice, Marisa Ioppolo-Armanios and Mark Jones also contributed to the writing of the paper.

CHAPTER 4

Samples were taken by Christiane D. Vitzthum von Eckstaedt. David Kerry helped with the biomass combustion sampling set up and provided facilities. Isotope and compound identification analyses were performed by Christiane D. Vitzthum von Eckstaedt. Christiane D. Vitzthum von Eckstaedt, Kliti Grice, Marisa Ioppolo-Armanios interpreted results, and Christiane D. Vitzthum von Eckstaedt wrote the paper. Kliti Grice, Marisa Ioppolo-Armanios provided intellectual input through discussions of results and also contributed to the writing of the paper.

Kliti Grice provided analytical facilities (ARC - LIEFP and ARC Discovery). The TD unit used in this project was supported by joint funding provided by Alcoa and WA-OIGC (Grice internal strategic grant). The project was funded by the Co-operative Research Centre for Contamination Assessment and Remediation of the Environment Pty Ltd. (CRC CARE) and managed by Kliti Grice.

SECONDARY PUBLICATIONS

Manuscripts and abstracts based on research that was conducted during the preparation of this thesis.

Peer-reviewed journal articles not part of thesis research

Abstracts

***** Directly related to PhD.

***Vitzthum von Eckstaedt C**, Grice K, Ioppolo-Armanios M, Jones M, Wang S (2007) Sourcing VOCs in industrial emissions by compound specific isotope analysis. "*23rd International Meeting of Organic Geochemistry*" (IMOG), Torquay, England, Sept. 2007. Poster, Book of Abstracts P312-WE, pp. 743-744.

Vitzthum von Eckstaedt C, Stalvies C, Brunstein B, Grice K, Volk H, Ross AS (2008) Partitioning and photo-oxidation experiments of Australian crude oils in seawater. "*15th Australian Organic Geochemistry Conference*" (AOGC), Adelaide, South Australia, September 2008. Poster, Book of Abstracts P21

***Vitzthum von Eckstaedt C**, Grice K, Chidlow G, Ioppolo-Armanios M, Jones M (2009) Method Development for sourcing VOCs using compound specific isotope analyses. "*3rd International Contaminated Site Remediation Conference*" (CleanUp09). Adelaide, South Australia, September 2009. oral, Book of Abstracts pp. 21-22

***Vitzthum von Eckstaedt C**, Grice K, Chidlow G, Ioppolo-Armanios M, Jones M (2009) Method development for compound specific isotope analysis (δD) of atmospheric VOCs. "*10th Australasian Environmental Isotope Conference & 3rd Australasian Hydrogeology Research Conference*" December 2009, Perth, Western Australia. oral, Book of Abstracts p. 50

Jaraula CMB, Grice K, **Vitzthum von Eckstaedt C**, Twitchett R, Wignall P, Kelly D 2010. Stable carbon and hydrogen isotopes of components derived from controlled burning experiments of C3 and C4 plants and their use as environmental proxies for tracking fire history. *Australian Organic Geochemistry Conference* (AOGC), December 2010, Canberra, ACT, oral, abstract book, pp. 62-63

Jaraula CMB, Grice K, **Vitzthum von Eckstaedt** C, Twitchett R, Wignall P, Kelly D 2010. Constraining stable carbon and hydrogen isotopes excursions of fire events from controlled burning experiments and applications to the Triassic-Jurassic extinction event. *The Australia and New Zealand Society for Mass Spectrometry 23 Biennial Conference* (ANZSMS), February 2011, Perth, Western Australia, oral, abstract book p. 45

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Chapter 1

Introduction

1.1 Volatile Organic Compounds

Volatile organic compounds (VOCs) are an important class of air pollutants, commonly found in the atmosphere mainly in urban and industrial areas. There is currently no global consistent definition of VOC. For example, the U.S. Environmental Protection Agency (EPA) describes a VOC as an organic compound that plays a critical role in photochemical reactions in the atmosphere (US-EPA, 2006). The European Environment Agency (EEA) describes a VOC as an organic compound that under typical conditions can vaporise into the atmosphere (EEA, 2011) (excluding CO, CO_2, carbonic acid, metallic carbides, carbonates ammonium carbonate and CH_4). Collectively VOCs are considered to be very important components due to their involvement in photochemical pollution and many are considered to be toxic, especially to humans. VOCs do not just occur in the atmosphere but are also of concern in ground and surface waters as well as soils (Siegrist, 1991; Lewis et al., 1994; Zoccolillo et al., 2005; Jochmann et al., 2006). Throughout this thesis the VOCs studied are referred to those present as hydrocarbons in the atmosphere ranging between C_6 and C_{10}, i.e. BTEX (benzene, toluene, ethylbenzene and xylene).

1.1.1 Environmentally Relevance

VOCs can have an influence on the environment and human health even at very low levels of exposure as shown in many epidemiological studies (WHO, 2000). VOCs can undergo photochemical reactions leading to ozone formation and thus enhancing the global greenhouse effect. Some VOCs can be also toxic or carcinogenic to humans and have the potential to accumulate and persist in the environment. Depression of the central nervous system is a common effect of most hydrocarbons. The hydrocarbons are lipid-soluble and dissolve in the membrane of nerve cells in the brain, perturbing their function. Benzene is toxic to organs like the bone marrow that form blood cells and can lead to the production of leukemia.

1.1.2 Sources of VOCs

VOCs are derived from non-combusted petroleum products or formed during combustion of organic material caused by either human processes or environmental events (i.e. bush/forest fire, oil seepage) or emitted by biogenic sources (plants and algae). The main anthropogenic sources include solvent use, processing of dyes and petroleum and traffic-related emissions. In addition VOCs can be derived from industrial processes. However, human related emissions are separated into either natural or synthetic sources depending on the kind of the raw material, i.e. natural sources include combustion products of crude oil, coal or wood (Baek et al., 1991; Harvey, 1997; Atkinson, 2000; Kansal, 2009).

The precise process leading to the formation of VOCs during combustion is not yet fully understood. It is known that they are established by a combination of cracking and formation of components which is dependent on the temperature and oxygen level(s). At higher temperatures organic compounds decay to smaller and more unstable components (via pyrolysis). These components exist predominantly as free radicals which are highly reactive and form aromatic hydrocarbons in subsequent reactions (pyrosynthesis) (Ballentine et al., 1996;

Mastral and Callen, 2000). A possible formation pathway of naphthalene is shown in **Figure 1.1** as an example.

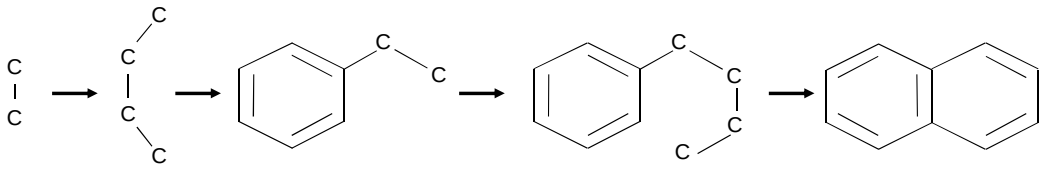


Figure 1.1: Formation of naphthalene

The C_2 fragment e.g. acetylene; C_4 fragments (e.g. vinylacetylene or 1,3-butadiene) can be the precursor(s) for styrene or ethylbenzene and intermediates for naphthalene. These compounds have been detected in emissions of combustion processes (Cole et al., 1984). During low temperature combustion (660 to 740 °C) alkyl-substituted aromatics are mainly formed whereas at higher temperatures (1.900 °C) polyaromatic hydrocarbons (PAHs) are produced (Richter and Howard, 2000; Lima et al., 2005). Industry processes generally use the same conditions so use constant temperatures. Thus the VOCs in the emission are mainly determined by the raw material whereas i.e. the emission composition of bushfires can vary greatly due to a wide range of combustion temperatures and oxygen levels.

1.1.3 Traditional Sampling Techniques used for VOCs

VOCs are object of research and environmental protection since the 1950s (Haagen-Smit et al., 1953; Harrison and Hester, 1995). A number of techniques have been used to collect airborne samples for qualitative and/or quantitative laboratory analysis (e.g. GC-MS). The choice of the sampling technique depends mainly on the research focus (e.g. complexity or restriction of the sample content), sampling point conditions and/or concentration specifications (Rudolph et al., 1990; Aragón et al., 2000; Czaplicka and Klejnowski, 2002; Demeestere et al., 2007; Kumar and Viden, 2007). Available resources or instrument compatibility might play a minor role.

(i) Sampling without pre-concentration

Whole air samples can be collected in different types of container e.g. evacuated stainless steel canisters, polymer bags (plastic or inert Teflon), gas tight syringes and glass container. A sample aliquot can be analysed later using GC, by direct injection or, more frequently, in combination with a pre-concentration step. Whole air sampling technique avoids the breakthrough (BT) of target compounds and provides multiple aliquots for replicate analysis and is widely used. However, the sampling amount is extremely limited and in addition, some VOCs, such as certain light alkenes and oxygenated VOCs are not stable in most canisters, which could cause isotopic fractionation. Stainless steel containers are labour intense and involves a complex cleaning procedure to avoid sample contamination. Polymer bags are inexpensive and easy to handle but even more restricted in sampling volume and show problems with substantial contamination and out gassing through the material.

(ii) Pre-concentration sampling

VOCs can be sampled and simultaneously pre-concentrated using an adsorptive material (Harper, 2000; Dettmer and Engewald, 2002, 2003; Woolfenden, 2010a, b). There are two different ways of concentrating VOCs on a sorbent – active and passive sampling. Passive sampling relies on the unassisted molecular diffusion of gaseous agents (analytes) through a diffusive surface onto an adsorbent. It operates without electricity or an additional devise (i.e. a pump) and is used for monitoring average pollution levels over time periods (i.e.at the work place or monitor personal exposure). Active solid sampling, is to pump a defined volume of air through a sorption tube (a short piece of tubing packed with the adsorbent). The process is comparable to frontal chromatography where the sampling efficiency relays on the retention capability of the adsorbent. Adsorbent materials can be highly selective in regards to adsorbed compounds. The sampling volume is essentially depending on the breakthrough volume (BTV) of the compounds of interest for the specific sorbent. The term specific BTV is defined as the volume of gas that causes a compound to migrate through an adsorbent bed (one gram adsorbent material) at a specific temperature. For every 10°C rise in temperature the capacity is

reduced by half starting from 40°C (US-EPA, 1999; Kroupa et al., 2004; Woolfenden, 2010b). The BTV depends also from the chemical composition and concentrations of the sample. The competitive effect between compounds on the adsorbent material was described by Peters and Bakkeren (1994) and Comes et al. (1993). Theoretical or lab based empirical approaches to determine the BTV for a certain concentration carries the difficulty to mimic the composition and the conditions of a real sample. Water or humidity content can have an impact on retention volume of certain adsorbent materials but there are also highly hydrophobic sorbents available, e.g. TenaxTA (Helmig and Vierling, 1995).

Adsorbent materials are commercially available in a large number. Criteria for the selection of an applicable sorbent are the complete enrichment of analytes depending on (i) sorbent strength; (ii) complete and fast desorption of the analytes; (iii) selectivity for compounds of interest; (iv) water affinity; (v) inert surface; (vi) low artefact formation; (vii) mechanical and thermal stability (Dettmer and Engewald, 2002, 2003). The most commonly used adsorbent materials can be classified in four groups a) activated carbon b) carbon molecular sieves c) graphitized carbon blacks and d) porous organic polymers.

In both pre-concentration techniques the sample is thermally desorbed at specific temperatures without causing decomposition but maintain complete desorption to be transferred in an inert gas (e.g. helium) into the analytical instrument (e.g. GC).

Tubes containing adsorbent material can be made of glass or (coated) stainless steel in various dimensions depending on the manufacturer and desorber's compatibility. Stainless steel tubes can be purchased with an inner coating (e.g. glass lined) or can obtain deactivated (silcosteel process) to reduce the metal reactivities with components. Tubes are packed with one or more adsorbent materials and held in place by with glass wool, wire gauze, or glass frits depending on the required desorption temperature conditions.

Multiple beds of adsorbents enable the analysis of a wider range of compounds in a single sampling step. The adsorbents are arranged in order of increasing adsorbent strength, from sample inlet to sample outlet (**Figure 1.2**).The largest molecules in the sample are trapped by the first adsorbent. Smaller molecules are trapped by the succeeding, stronger beds. The choice of combination of the adsorbent depends on the desorption temperature. The adsorbent material with the lowest desorption temperature can restrict the desorption process. This temperature of desorption must be sufficient to ensure complete desorption of compounds of interest on all adsorbents in the tube.

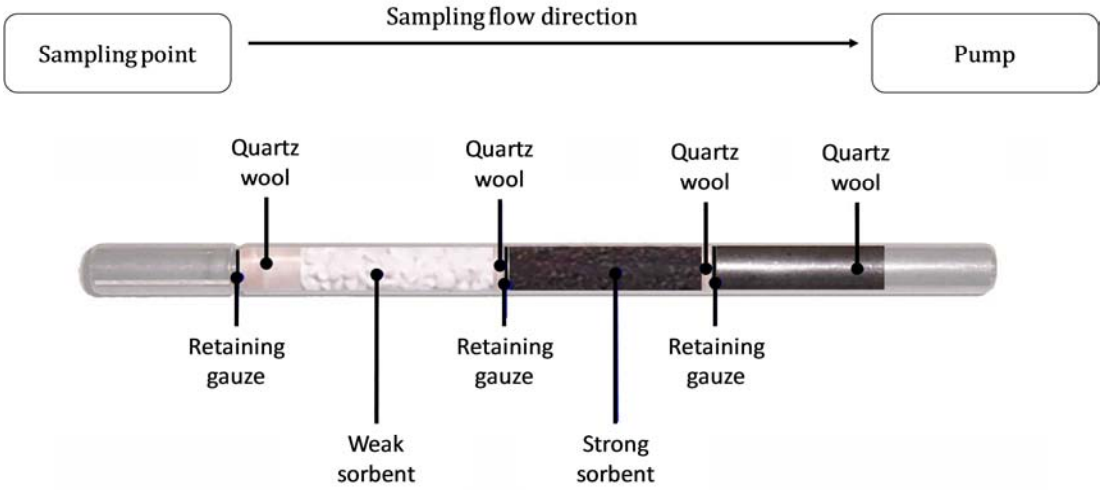


Figure 1.2: Schematic of a TD tube with multiple adsorbent materials

The resin chosen for the experimental work in this thesis needed to be suitable for trapping VOCs in a range of C_6 to C_{10} with boiling points spanning between 80°C and 220°C. Furthermore a very low affinity for water was a critical parameter to consider because hydrogen gas (H_2, DH) can be generated from water via pyrolysis of compounds within the GC-irMS furnace. The hydrogen generated could strongly compromise the stable hydrogen isotope analyses of VOCs. The adsorbent TenaxTA fulfilled these requirements. A combination of other sorbents in a multibed tube was not necessary. TenaxTA is a porous polymer resin based on 2,6-diphenylene oxide. It is suitable for adsorption and analysis of a range of volatile and semi-volatile organic compounds >C_6 and is

often used for collecting VOCs from air samples (Clément et al., 2000; Hippelein, 2004).

1.1.4 Thermal Desorption Instruments for GC analysis

Today's commercially available thermal desorption (TD) units for compounds adsorbed on solid sorbents vary in configurations and techniques. Short Path TD units are single stage desorbers transferring the desorbed sample directly into the GC injection port using a syringe like attachment for a short length of sample transport (Peng and Batterman, 2000; Kuntasal et al., 2005). The short transport distance minimises the risk of contamination and/or developing cold spots. Other single stage desorbers are equipped with a downstream cryogenic trap to re-focus the desorbed sample in a glass liner before the sample reaches the analytical GC column. Other TD units refocusing the sample on a secondary cooled tube which is also filled with an adsorbent material (2 stage TD units). The re-focusing step improves chromatographically separation of the compounds. A device for quantitative re-collection of the split flow on a separate sample tube has only been offered by a few TD manufacturers. Thus the split sample provides a replicate of the injected sample which can be used for further analysis and saves important sampling time and resources (**Figure 2.1**). Most TD units are available in either single tube (manual) or automated multi tube desorption systems.

1.2 Stable Isotopes

Stable isotopes as contrasting to radio (unstable) isotopes do not decay, thus their natural abundances stay relatively constant (**Table 1.1**).

Table 1.1: Natural abundance (atom %) of common stable isotopes

Carbon	Hydrogen	Oxygen	Sulfur	Nitrogen
^{12}C (98.899)	^{1}H (99.985)	^{16}O (99.759)	^{32}S (95.018)	^{14}N (99.9634)
^{13}C (1.1110)	D (^{2}H) (0.0105)	^{17}O (0.0374)	^{34}S (4.2150)	^{15}N (0.36630)
		^{18}O (0.2039)		

Stable isotope analysis relates to the mass difference between stable isotopes of the same element and measures their abundance as a ratio of the isotopes relative to a standard. Stable isotopic compositions are expressed by a delta notation in per mil (‰) enabling the expression of very small changes in isotopic ratios (Equ. 1.1).

$$\delta_{sample} = \left[\frac{R_{sample}}{R_{standard}} - 1\right] * 1000\ ‰\ (\text{per mil}) \qquad \text{(Equ. 1.1)}$$

R is the ratio of heavy isotope (*i.e.* ^{13}C) to light isotope (*i.e.* ^{12}C) measured in a sample relative to an international standard. Stable carbon isotopic analyses are relative to the international Vienna Pee Dee Belemnite ('VPDB') marine limestone standard, calibrated to the first marine limestone from the Pee Dee formation in South Carolina (USA). This standard is nowadays used up and has been replaced by calibrating another carbonate (NBS-19) relative to PDB (Urey et al., 1951; Craig, 1957). The latest calibration scale is called 'VPDB' (Vienna PDB). For stable hydrogen isotopic composition, D/H is relative to the Standard Mean Ocean Water (SMOW). However, this standard is also no longer accessible as a reference material, and therefore was defined relative to an additional water standard (NBS-1, also exhausted) (Werner and Brand, 2001). Therefore a novel reference material was developed with an isotopic composition corresponding to that of SMOW, which has led to the existing 'VSMOW' (Vienna SMOW) scale. Positive δ values represent an enrichment of the heavy isotope

relative to the international standard, while negative values represent a depletion of the heavy isotope.

Isotopes of an element have a different atomic mass which causes differences in the physical and chemical properties of compounds with different isotopic contents (e.g. isotopologues). Heavy isotopes undergo all of the same chemical reactions as light isotopes, but, simply because they are heavier, they do it ever so slightly slower leading to different preferences during chemical and physical reactions the so called 'isotopic fractionation'. In a closed systems 'isotopic fractionation' can occur as a result of temperature-reliant equilibrium isotope-exchange reactions leading to a change of the isotope distribution between different chemicals, phases, or even between individual molecules (Hoefs, 1987) (equilibrium isotope effects). The impact of isotopic fractionation usually increases when an irreversible chemical/physical reaction takes place resulting in a change in the chemical system, for example, the water vapour is removed before condensation (kinetic isotope effect). In theory, the rate determining step involves the cleavage of a bond. It is easier to cleave the bonds of molecules that contain the lighter isotopes, because the vibration frequency of such bonds is somewhat elevated. The change in isotopic composition can reveal the fate of a compound or connects the compound to its source material (Baek et al., 1991; Slater, 2003) (**Figure 1.3** and **Figure 1.4**).

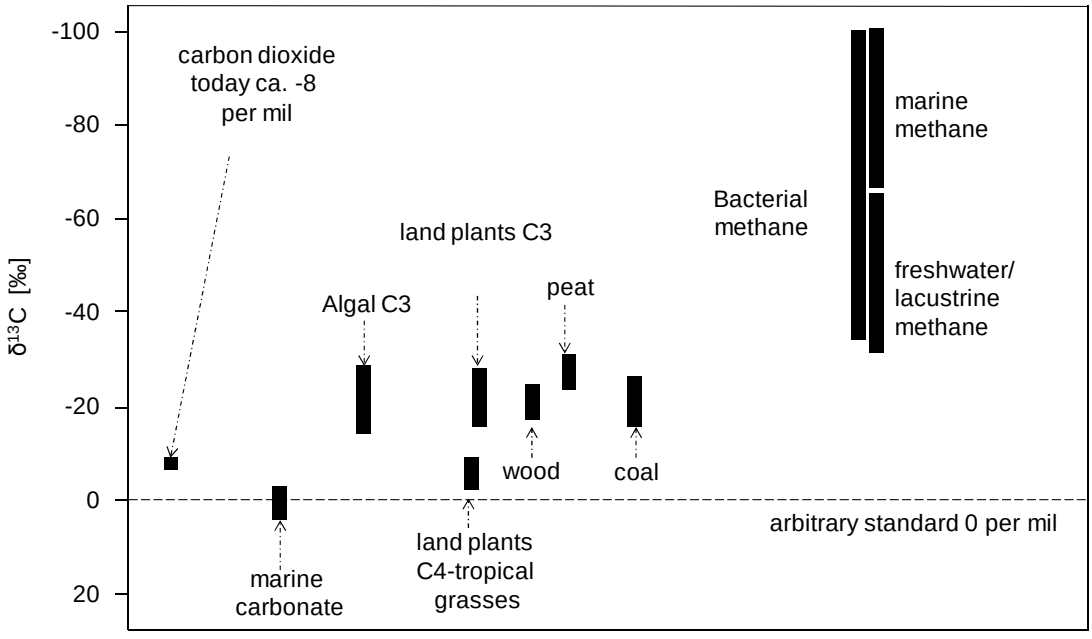


Figure 1.3: Natural variations in stable carbon isotope values (after Grice, lecture slides Curtin University)

The two stable isotopes of hydrogen have the largest mass difference (~2) of all elements and therefore show the largest effect when i.e. the lighter isotope (H) is exchanged with the heavier (D). Therefore analysing δD is a powerful tool where other stable isotope differences are negligible. However, D/H analysis requires an increased sample size compared to $^{13}C/^{12}C$ analysis due to the low natural abundance of deuterium (**Table 1.1**) and that two moles of H are required for each mole of sample gas (H_2) (Sessions, 2006).

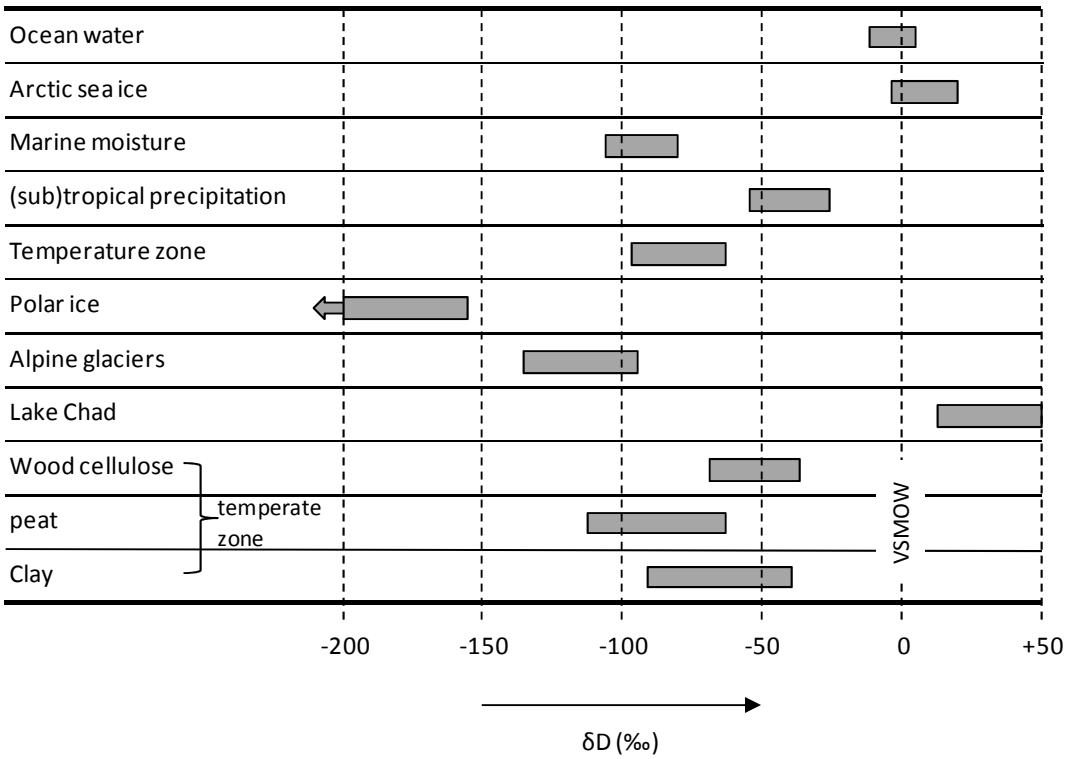


Figure 1.4: General view of D/H variations in natural compounds. The ranges are indicative for the majority of materials shown (after „Global cycle of water", IAEA).

1.3 Compound Specific Isotope Analysis (CSIA)

The development of gas chromatography isotope ratio mass spectrometry (GC-irMS) for compound specific isotope analysis (CSIA) has allowed the stable isotope analysis of various individual components in a complex mixture

(Matthews and Hayes, 1978; Burgøyne and Hayes, 1998). For $\delta^{13}C$ analysis the combustion interface can consist of a quartz tube packed with CuO pellets (heated at 850°C) or a ceramic tube holding entwined wires of CuO/Pt (850°C) (Matthews and Hayes, 1978; Hayes, 1983) to yield CO_2 and H_2O for each GC-separated component. H_2O is then removed with liquid N_2 maintained at -100°C and/or a Nafion H_2O trap. The isotope ratio mass spectrometer can measure the abundances of the ions masses 44, 45 and 46 (see **Figure 2.3**). The development of D/H measurements was marketable around 10 years after carbon stable isotope analysis was established. To convert chromatographically separated compounds into H_2 molecules the sample needs to be pyrolysed before entering the isotope ratio mass spectrometer. The pyrolysis furnace contains either a ceramic tube covered with a glassy carbon coating (1400°C) or a quartz tube containing chromium pellets as a reactant (1050°C) (e.g. Prosser and Scrimgeour, 1995; Burgøyne and Hayes, 1998) (see **Figure 2.2**). A problem, unique for D/H analyses by GC-IRMS, is the presence of a $^4He^+$ ion beam, arising from the carrier gas. Large amounts of helium result in ion collisions in the ion source which causes an energy loss of $^4He^+$ corrupting the measurement of the very weak HD beam at mass 3. Hilkert et al. (1999) modified the ion beam collector to compensate the interference of helium ions. Measured D/H ratios have to be corrected for the presence of the interfering isobars H_3^+. H_2 in the IRMS ion source reacts to form H_3^+ (Equ. 1.2).

$$H_2^+ + H_2 \rightarrow H_3^+ + H^* \qquad \text{(Equ. 1.2)}$$

Sessions et al. (2001) established a method to determine the abundance of H_3^+ ion on a daily basis to correct for its impact on the compound values by introducing a series of reference gas peaks of identical isotope composition but varying amplitude. The result from this manually initiated H_3^+ correction is automatically implied in the data processing of the instrument software.

CSIA offers a much greater level of detail compared to bulk analysis. Bulk analysis provides the average value of all of the components present in the material analysed. CSIA ($\delta^{13}C$ and δD) today is used in a range of diverse research fields

e.g. in organic geochemical research (Hayes et al., 1990; Grice et al., 1998; Peters et al., 2005; Schimmelmann et al., 2006; Grice et al., 2007); environmental investigations (McRae et al., 2000; Rudolph et al., 2002; Slater, 2003; Pilgrim et al., 2010), also it has been recently applied to paleoclimate (e.g. char and ash analysis from plant combustion). The application of CSIA for $\delta^{13}C$ has increased the likelihood to distinguish between a range of natural materials (Mancini et al., 2008; O'Sullivan and Kalin, 2008). However, source delineation depends largely on individual conditions such as locality, climate and the δ values of the source(s).

1.4 VOCs and Stable Isotopes

Most of the research on atmospheric VOCs done thus far has focused on carbon stable isotopes (Goldstein, 2003). Other elements have not been reported for atmospheric VOCs, except analysing δD of formaldehyde (Rice and Quay, 2009). Rudolph at al. (1997) was pioneer applying CSIA ($\delta^{13}C$) to light non-methane hydrocarbons (NMHC) and chloromethane in the atmosphere at ppt levels. Other followed and investigated different ranges of VOCs (Nara et al., 2005; Iannone et al., 2007; Redeker et al., 2007). $\delta^{13}C$ values of NMHC in further emission sources have been determined e.g. from *n*-alkanes and benzene in traffic, coal combustion and cooking exhaust emissions in China (Peng et al. 2009) and Toronto (Rudolph et al. 2002). Oxygenated VOCs were recently investigated (Giebel et al., 2010) and a clear distinction was observed between $\delta^{13}C$ of emissions released from plants and automobiles. Czapiewski et al. (2002) reported the isotopic composition of non-methane hydrocarbons in emissions from biomass burning (C3 plants).

As described above (1.1.4) VOCs have been a topic of interest in various research studies where TD is an established technique (Woolfenden, 2010a, Dettmer and Engewald, 2003, Ras-Mallorqui et al., 2007). Previously TD has also been applied to CSIA using a short path TD unit to analyse $\delta^{13}C$ of low-molecular-weight VOCs and confirmed the general suitability of TD-GC-irMS (Turner et al., 2006; Peng et al., 2009). Although Turner et al. (2006) showed

that the differences between $\delta^{13}C$ values of VOCs in an industry emission compared to those from a car exhaust were negligible. Using stable isotopes analysis of two elements (C and H) increases the potential to establish significant isotopic differences, e.g. shown by Sun et al. where the source of polycyclic aromatic hydrocarbons (PAHs) were effectively distinguished when applying $\delta^{13}C$ and δD analysis (Sun et al., 2003)(**Figure 1.5**).

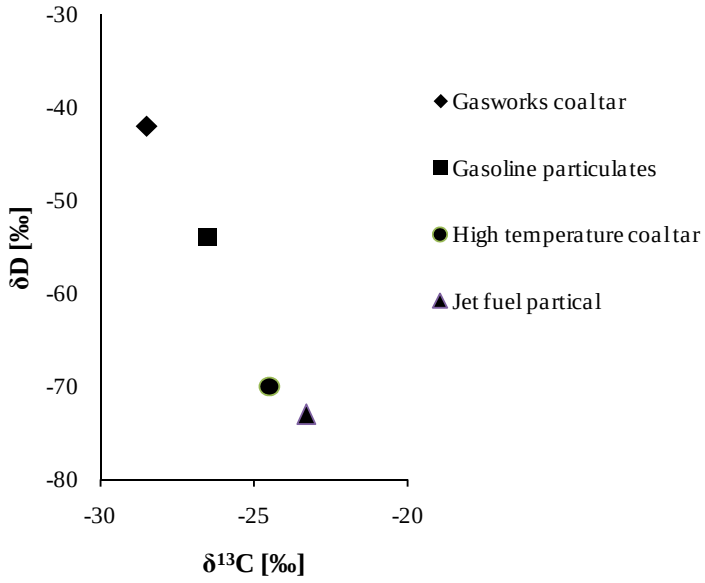
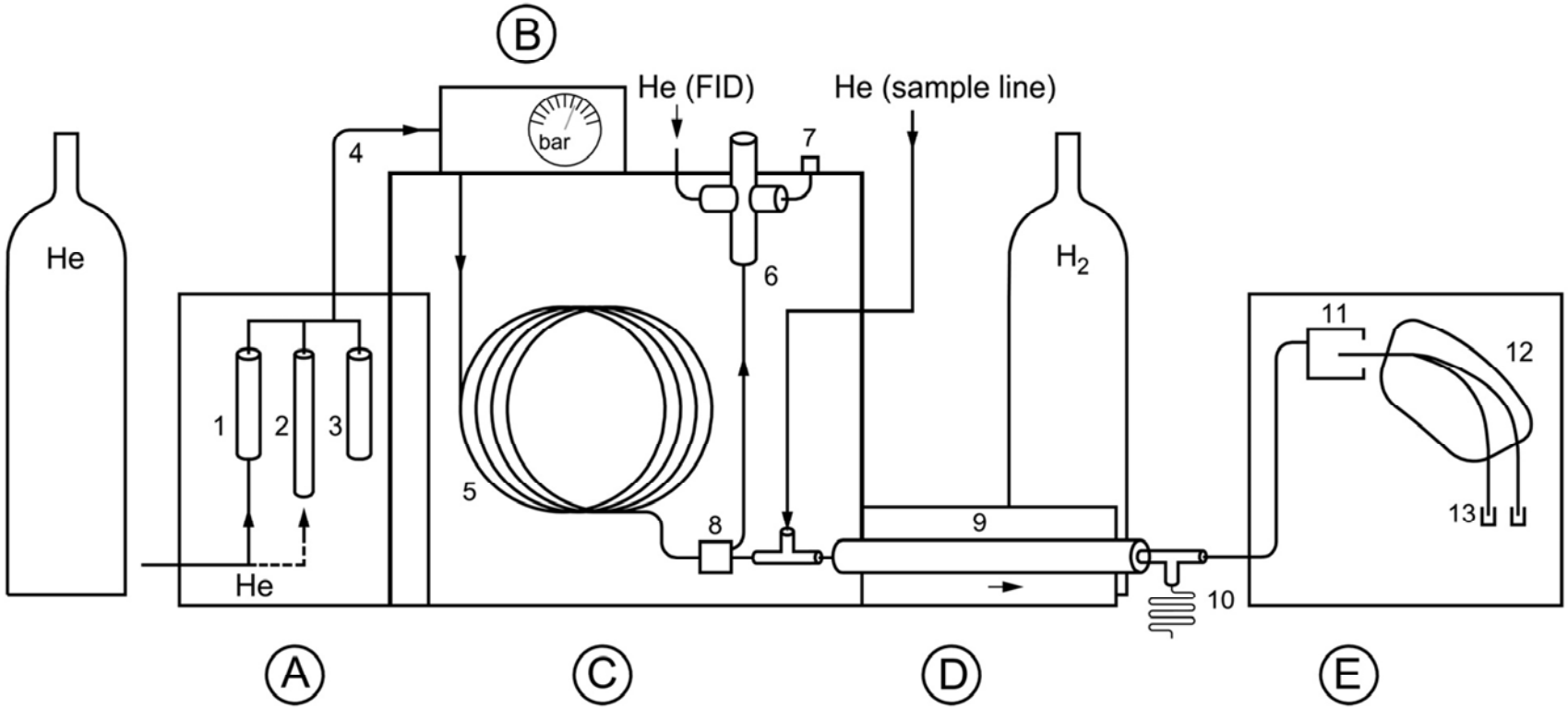


Figure 1.5: Correlation of $\delta^{13}C$ and δD for selected PAHs generated by different combustion processes (after Sun et al., 2003)

A schematic of the analytical instrumental set-up used for this research is illustrated in **Figure 1.6** where a 2 stage TD unit was connected to a GC-irMS (for stable hydrogen isotope analysis). In the GC cabinet, a system of capillaries and valves enables diversion of the sample either to the FID or to the combustion interface. The arrangement of capillaries within the GC cabinet is shown in **Figure 1.6**. One end of the GC capillary column is connected to the transfer line of the TD unit by a press fit connector. The other end of the GC column passes into a splitter union (VSOS splitter) from which two fused silica capillaries emerge. The first capillary runs from the splitter union to the heart split (HS) valve which is positioned near the FID. The HS valve is a needle valve containing a back drilled ferrule. The second capillary runs through the zero dead volume reducer assembly fixed to the end of the quartz furnace tube. The

section of the second capillary sitting within the furnace tube has the outer polyamide coating removed. The HS operates both pneumatically and via helium flow and pressure to divert the sample flow either into the irMS (closed HS) or to the FID (open HS). Helium enters the GC column through the TD unit gas supply. Additionally helium enters the furnace tube (upstream) at zero dead volume union as sample line (SLN) helium, and at the HS valve as FID helium. The pressure of the SLN helium is greater than the FID helium and the pressure of helium at the end of the GC column. Thus, there is a small flow of helium from the furnace tube to the splitter union and from the splitter union to the HS valve. When the HS valve is open the pressure of the SLN helium prevents the sample flow from passing towards the pyrolysis reactor. The GC flow therefore passes towards the HS valve, and hence to the FID. When the HS valve is closed the GC flow is mechanically prevented from passing through to the FID. The pressure of the VSOS splitter eventually exceeds the SLN helium pressure and the sample flows into the reactor interface to the irMS detector. The HS mechanism enables the diversion of the solvent (liquid injections) and/or compounds in concentration above instrument requirements. A large quantity of solvent exhausts the furnace reactants causing incomplete combustion and a contamination of the ion source. The HS mechanism also enables the introduction of the reference gas into the mass spectrometer on a clean background since it eliminates a co-elution with peaks from the sample preparation system.



A - thermal desorption unit
B - pressure gauge
C - gas chromatography
D - pyrolysis reactor
E - isotope ratio MS

1 – sampling tube
2 – cold trap
3 – split flow tube
4 – transfer line
5 – GC-column

6 – heartsplit valve
7 – FID
8 – VSOS splitter
9 – quartz tube with chromium
10 – open split

11 - electron impact ionization source
12 - magnetic-sector mass analyser
13 - H_2 detectors

Figure 1.6: Schematic of instrumental set up of TD-GC-irMS measurements

1.5 Isotopic Fractionation of VOCs

1.5.1 Condensation/ Evaporation

Given the volatility of the compounds in this study the impact of condensation / evaporation on isotopic fractionation will be discussed in this section.

Laboratory studies for hydrocarbons, e.g. *n*-alkanes and aromatics, have shown that stable carbon isotope signatures do not fractionate significantly (>0.5‰) during vaporisation (Harrington et al., 1999; Slater et al., 2000).

In contrast significant isotopic fractionation of stable hydrogen isotopes in hydrocarbons was observed in a few studies but only at high levels of vaporisation (>75 %) (Wang and Huang, 2001, 2003). Wang and Huang (2001, 2003) discovered also that alcohols show a different direction of isotopic fractionation than e.g. *n*-alkanes and aromatics (Table 1.2). The residual liquids of alcohols get heavier (enriched in D) compared to the gas during evaporation, but δD values of *n*-alkanes and aromatics are getting lighter (depleted in D) in the remaining liquid. This can be explained different bond forces of the mentioned compound groups. Every hydrocarbon in the liquid phase experiences weak intermolecular bonds (van der Waals forces). These need to be overcome for the hydrocarbon to evaporate. The van der Waals binding energy decreases with increasing number of D in the molecule which results in lower boiling points and lower vapour pressure compared to molecules with the lighter H atom. The vapour phase becomes enriched in D during evaporation. Compounds with heteroatoms like ketones or alcohols form hydrogen bonds which are stronger than van der Waals bonds. The bonding energy of H-bonds increases with increasing number of D resulting in a higher boiling point. This effect is dominant over the opposite effect of mass difference described above. Therefore, compounds which form H-bonds become enriched in δD in the liquid phase during evaporation.

Table 1.2: H isotope fractionation of common VOCs during vaporization (Wang and Huang, 2001, 2003)

compounds	ΔδD	remaining liquid
ALCOHOLS		
methanol	89.2 ‰	12.4 %
ethanol	60.1 ‰	11.2 %
n-ALKANES		
C7	14.3 ‰	20.4 %
C8	11.0 ‰	20.4 %
C9	7.2 ‰	20.4 %
AROMATICS		
benzene	7.7 ‰	4.9 %
toluene	18.4 ‰	10.2 %
ethylbenzene	44.5 ‰	5.3 %
p-xylene	29.5 ‰	3.1 %
o-xylene	27.2 ‰	5.8 %

Summarising the impact of volatilisation on the isotopic signature of VOCs, it plays only a significant role for stable hydrogen isotopes when more than 75 % of the compound evaporates.

1.5.2 Adsorption

Harrington et al. (1999) described HPLC experiments with ^{13}C-labeled compounds and suggested that C isotope fractionation during adsorption of unlabeled benzene and toluene in natural environments will be negligible, But they pointed out that with increasing instrument precision of CSIA a very small C isotope fractionation may be quantifiable in the future.

Sorption experiments onto activated carbon by Schüth et al. (2003) revealed no significant fractionation neither for carbon nor for hydrogen isotopes of BTEX compounds.

However experiments were carried out to prove that also the adsorption – desorption process described in this thesis is not causing isotopic fractionation (C and H) (see 2.3.3)

1.6 Aims of this Thesis

This thesis brings together two analytical methods (TD and CSIA) for establishing the source of VOCs from a series of emissions. TD-GC-irMS was thoroughly investigated for analysing compound specific δD and $\delta^{13}C$ of atmospheric VOCs ranging between C_6-C_{10} using TenaxTA as an adsorbent resin. Essential aspects of the technique needed to be evaluated, e.g. influence of background water, sample break through (BT) and storage behavior on the isotope ratio of collected VOCs. This would be the first time that compound specific $\delta^{13}C$ values are reported in combination with δD values using TD-GC-irMS. δ values (C and H) of VOCs derived from industry and car exhaust emissions as well as those derived from plant combustion (C3 and C4 plants) were analysed to establish any significant isotopic distinction between these sources using the developed method.

1.7 References

Aragón, P., Atienza, J., Climent, M., 2000. Analysis of organic compounds in air: A review. *Critical Reviews in Analytical Chemistry.* 30, 121-151.

Atkinson, R., 2000. Atmospheric chemistry of VOCs and NO_x. *Atmospheric Environment*. 34, 2063-2101

Baek, S., Field, R., Goldstone, M., Kirk, P., Lester, J., Perry, R., 1991. A review of atmospheric polycyclic aromatic hydrocarbons: sources, fate and behavior. *Water, Air, & Soil Pollution.* 60, 279-300.

Ballentine, D., Macko, S., Turekian, V., Gilhooly, W., Martincigh, B., 1996. Compound specific isotope analysis of fatty acids and polycyclic aromatic hydrocarbons in aerosols: implications for biomass burning. *Organic Geochemistry.* 25, 97-104.

Burgøyne, T., Hayes, J., 1998. Quantitative production of H_2 by pyrolysis of gas chromatographic effluents. *Analytical Chemistry.* 70, 5136-5141.

Clément, M., Arzel, S., Le Bot, B., Seux, R., Millet, M., 2000. Adsorption/thermal desorption-GC/MS for the analysis of pesticides in the atmosphere. *Chemosphere.* 40, 49-56.

Cole, J.A., Bittner, J.D., Longwell, J.P., Howard, J.B., 1984. Formation mechanisms of aromatic compounds in aliphatic flames. *Combustion and Flame.* 56, 51-70.

Comes, P., Gonzalez-Flesca, N., Menard, T., Grimalt, J., 1993. Langmuir-derived equations for the prediction of solid adsorbent breakthrough volumes of volatile organic compounds in atmospheric emission effluents. *Analytical Chemistry.* 65, 1048-1053.

Craig, H., 1957. Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analysis of carbon dioxide. *Geochimica et Cosmochimica Acta.* 12, 133-149.

Czaplicka, M., Klejnowski, K., 2002. Determination of volatile organic compounds in ambient air comparison of methods. *Journal of Chromatography A.* 976, 369-376.

Demeestere, K., Dewulf, J., De Witte, B., Van Langenhove, H., 2007. Sample preparation for the analysis of volatile organic compounds in air and water matrices. *Journal of Chromatography A.* 1153, 130-144.

Dettmer, K., Engewald, W., 2002. Adsorbent materials commonly used in air analysis for adsorptive enrichment and thermal desorption of volatile organic compounds. *Analytical and Bioanalytical Chemistry.* 373, 490-500.

Dettmer, K., Engewald, W., 2003. Ambient air analysis of volatile organic compounds using adsorptive enrichment. *Journal of Chromatography A.* 57, 339-347.

European Environment Agency, 2011. Environmental Terminology and Discovery Service (ETDS) http://glossary.eea.europa.eu/terminology/concept_html?term=voc.

Giebel, B., Swart, P., Riemer, D., 2010. $\delta^{13}C$ stable isotope analysis of atmospheric oxygenated volatile organic compounds by gas chromatography-isotope ratio mass spectrometry. *Analytical Chemistry.* 82, 6797–6806.

Goldstein, A., Shaw, S., 2003. Isotopes of volatile organic compounds: An emerging approach for studying atmospheric budgets and chemistry. *Chemical Reviews.* 103, 5025-5048.

Grice, K., Nabbefeld, B., Maslen, E., 2007. Source and significance of selected polycyclic aromatic hydrocarbons in sediments (Hovea-3 well, Perth Basin, Western Australia) spanning the Permian-Triassic boundary. *Organic Geochemistry.* 38, 1795-1803.

Grice, K., Schouten, S., Peters, K., Sinninghe Damsté, J., 1998. Molecular isotopic characterisation of hydrocarbon biomarkers in Palaeocene–Eocene evaporitic, lacustrine source rocks from the Jianghan Basin, China. *Organic Geochemistry.* 29, 1745-1764.

Haagen-Smit, A.J., Bradley, C.E., Fox, M.M., 1953. Ozone formation in photochemical oxidation of organic substances. *Industrial and Engineering Chemistry.* 45, 2086–2089.

Harper, M., 2000. Sorbent trapping of volatile organic compounds from air. *Journal of Chromatography A*. 885, 129-151.

Harrington, R., Poulson, S., Drever, J., Colberg, P., Kelly, E., 1999. Carbon isotope systematics of monoaromatic hydrocarbons: vaporization and adsorption experiments. Organic Geochemistry 30, 765-775.

Harvey, R.G., 1997. Polycyclic aromatic hydrocarbons. Wiley-VCH, Inc., New York.

Hayes, J., Freeman, K., Popp, B., Hoham, C., 1990. Compound-specific isotopic analyses: A novel tool for reconstruction of ancient biogeochemical processes. *Organic Geochemistry.* 16, 1115–1128.

Helmig, D., Vierling, L., 1995. Water adsorption capacity of the solid adsorbents Tenax TA, Tenax GR, Carbotrap, Carbotrap C, Carbosieve SIII, and Carboxen 569 and water management techniques for the atmospheric sampling of volatile organic trace gases. *Analytical Chemistry.* 67, 4380-4386.

Hilkert, A., Douthitt, C., Schluter, H., Brand, W., 1999. Isotope ratio monitoring gas chromatography/mass spectrometry of D/H by high temperature conversion isotope ratio mass spectrometry. *Rapid Communications in Mass Spectrometry.* 13, 1226-1230

Hippelein, M., 2004. Background concentrations of individual and total volatile organic compounds in residential indoor air of Schleswig-Holstein, Germany. *Journal of Environmental Monitoring.* 6, 745.

Iannone, R., Koppmann, R., Rudolph, J., 2007. A technique for atmospheric measurements of stable carbon isotope ratios of isoprene, methacrolein, and methyl vinyl ketone. *Journal of Atmospheric Chemistry.* 58, 181-202.

Jochmann, M., Blessing, M., Haderlein, S., Schmidt, T., 2006. A new approach to determine method detection limits for compound-specific isotope analysis of volatile organic compounds. *Rapid Communications in Mass Spectrometry*. 20, 3639-3648.

Kansal, A., 2009. Sources and reactivity of NMHCs and VOCs in the atmosphere: A review. *Journal of Hazardous materials.* 166, 17-26.

Kroupa, A., Dewulf, J., Van Langenhove, H., Víden, I., 2004. Breakthrough characteristics of volatile organic compounds in the -10 to +170° C temperature range on Tenax TA determined by microtrap technology. *Journal of Chromatography A.* 1038, 215-223.

Kumar, A., Viden, I., 2007. Volatile organic compounds: Sampling methods and their worldwide profile in ambient air. *Environmental Monitoring and Assessment.* 131, 301-321.

Kuntasal, Ö., Karman, D., Wang, D., Tuncel, S., Tuncel, G., 2005. Determination of volatile organic compounds in different microenvironments by multibed adsorption and short-path thermal desorption followed by gas chromatographic–mass spectrometric analysis. *Journal of Chromatography A.* 1099, 43-54.

Lewis, T.E., Crockett, A.B., Siegrist, R.L., 1994. Soil sampling and analysis for volatile organic compounds. *Environmental Monitoring and Assessment.* 30, 213-246.

Lima, A.L.c.C., Farrington, J.W., Reddy, C.M., 2005. Combustion derived polycyclic aromatic hydrocarbons in the environment - A review. *Environmental Forensics.* 6, 109-131.

Mancini, S.A., Lacrampe-Couloume, G., Sherwood-Lollar, B., 2008. Source differentiation for benzene and chlorobenzene groundwater contamination: A field application of stable carbon and hydrogen isotope analyses. *Environmental Forensics.* 9, 177-186.

Mastral, A.M., Callen, M.S., 2000. A review on polycyclic aromatic hydrocarbon (PAH) emissions from energy generation. *Environmental Science and Technology.* 34, 3051-3057.

Matthews, D., Hayes, J., 1978. Isotope-ratio-monitoring gas chromatography-mass spectrometry. *Analytical Chemistry.* 50, 1465-1473.

McRae, C., Snape, C., Sun, C., Fabbri, D., Tartari, D., Trombini, C., Fallick, A., 2000. Use of compound-specific stable isotope analysis to source anthropogenic natural gas-derived polycyclic aromatic hydrocarbons in a lagoon sediment. *Environmental Science & Technology.* 34, 4684-4686.

Nara, H., Nakagawa, F., Yoshida, N., 2005. Development of two-dimensional gas chromatography/isotope ratio mass spectrometry for the stable carbon isotopic analysis of C_2-C_5 non-methane hydrocarbons emitted from biomass burning. *Rapid Communications in Mass Spectrometry.* 20, 241-247.

O'Sullivan, G., Kalin, R., 2008. Investigation of the range of carbon and hydrogen isotopes within a global set of gasolines. *Environmental Forensics.* 9, 166-176.

Peng, C.-Y., Batterman, S., 2000. Performance evaluation of a sorbent tube sampling method using short path thermal desorption for volatile organic compounds. *Journal of Environmental Monitoring.* 2, 313-324.

Peters, K.E., Walters, C.C., Moldowan, J.M., 2005. The Biomarker Guide, 2nd ed. Cambridge University Press, Cambridge.

Peters, R., Bakkeren, H., 1994. Sorbents in sampling. Stability and breakthrough measurements. *The Analyst*. 119, 71-74.

Pilgrim, T.S., Watling, R.J., Grice, K., 2010. Application of trace element and stable isotope signatures to determine the provenance of tea (Camellia sinensis) samples. *Food Chemistry.* 118, 921-926.

Prosser, S.J., Scrimgeour, C.M., 1995. High-precision determination of $^2H/^1H$ in H_2 and H_20 by continuous-flow isotope ratio mass spectrometry. *Analytical Chemistry.* 67, 1992-1997.

Ras-Mallorqui, M., Marce-Recasens, R., Borrull-Ballarin, F., 2007. Determination of volatile organic compounds in urban and industrial air from Tarragona by thermal desorption and gas chromatography–mass spectrometry. *Talanta.* 72, 941-950.

Redeker, K.R., Davis, S., Kalin, R.M., 2007. Isotope values of atmospheric halocarbons and hydrocarbons from Irish urban, rural, and marine locations. *Journal of Geophysical Research.* 112, D16307.

Rice, A.L., Quay, P.D., 2009. Isotopic composition of formaldehyde in urban air. *Environmental Science & Technology.* 43, 8752–8758.

Richter, H., Howard, J., 2000. Formation of polycyclic aromatic hydrocarbons and their growth to soot - a review of chemical reaction pathways. *Progress in Energy and Combustion Science.* 26, 565-608.

Rudolph, J., Czuba, E., Norman, A., Huang, L., Ernst, D., 2002. Stable carbon isotope composition of non-methane hydrocarbons in emissions from transportation related sources and atmospheric observations in an urban atmosphere. *Atmospheric Environment.* 36, 1173-1181.

Rudolph, J., Lowe, D., Martin, R., Clarkson, T., 1997. A novel method for compound specific determination of $\delta^{13}C$ in volatile organic compounds at ppt levels in ambient air. *Geophysical Research Letters.* 24, 659-662.

Rudolph, J., Müller, K., Koppmann, R., 1990. Sampling of organic volatiles in the atmosphere at moderate and low pollution levels. *Analytica Chimica Acta.* 236, 197-211.

Schimmelmann, A., Sessions, A.L., Mastalerz, M., 2006. Hydrogen isotopic (D/H) composition of organic matter during diagenesis and thermal maturation. *Annual Review of Earth and Planetary Sciences.* 34, 501-533.

Schüth, C., Taubald, H., Bolaño, N., Maciejczyk, K., 2003. Carbon and hydrogen isotope effects during sorption of organic contaminants on carbonaceous materials. Journal of Contaminant Hydrology 64, 269-281.

Sessions, A., Burgoyne, T., Hayes, J., 2001. Correction of H_3^+ contributions in hydrogen isotope ratio monitoring mass spectrometry. *Analytical Chemistry.* 73, 192-199.

Sessions, A.L., 2006. Isotope-ratio detection for gas chromatography. *Journal of Separation Science.* 29, 1946-1961.

Siegrist, R.L., 1991. Volatile organic compounds in contaminated soils: the nature and validity of the measurement process. *Journal of Hazardous materials.* 29, 3-15.

Slater, G.F., 2003. Stable isotope forensics - When isotopes work. *Environmental Forensics*. 4, 13-23.

Slater, G.F., Ahad, J.M.E., Sherwood-Lollar, B., Allen-King, R., Sleep, B., 2000. Carbon isotope effects resulting from equilibrium sorption of dissolved VOCs. Analytical Chemistry 72, 5669-5672.

Sun, C., Cooper, M., Snape, C.E., 2003. Use of compound-specific $\delta^{13}C$ andδD stable isotope measurements as an aid in the source apportionment of polyaromatic hydrocarbons. *Rapid Communications in Mass Spectrometry.* 17, 2611-2613.

Turner, N., Jones, M., Grice, K., Dawson, D., Ioppolo-Armanios, M., Fisher, S., 2006. $\delta^{13}C$ of volatile organic compounds (VOCs) in airborne samples by

thermal desorption-gas chromatography-isotope ratio-mass spectrometry (TD-GC-irMS). *Atmospheric Environment.* 40, 3381-3388.

Urey, H.C., Lowenstam, H.A., Epstein, S., McKinney, C.R., 1951. Measurement of palaeotemperatures and temperatures of the upper Cretaceous of England, Denmark, and Southeastern United States. *American Association of Petroleum Geologists Bulletin.* 62, 399-416.

US-EPA, 1999. Determination of volatile organic compounds in ambient air using active sampling onto sorbent tubes (Method TO-17). Compendium of methods for the determination of toxic organic compounds in ambient air. 2nd ed. U.S. Environmental Protection Agency (EPA), Cincinnati

U.S. Environmental Protection Agency, 2006. Terms of environment <http://www.epa.gov/OCEPAterms/vterms.html>.

Wang, Y., Huang, Y., 2001. Hydrogen isotope fractionation of low molecular weight *n*-alkanes during progressive vaporization. Organic Geochemistry 32, 991-998.

Wang, Y., Huang, Y., 2003. Hydrogen isotopic fractionation of petroleum hydrocarbons during vaporization: implications for assessing artificial and natural remediation of petroleum contamination. Applied Geochemistry 18, 1641-1651.Harrison, R.M., Hester, R.E., 1995. Volatile organic compounds in the atmosphere. The Royal Society of Chemistry. 1-106.

Werner, R.A., Brand, W.A., 2001. Referencing strategies and techniques in stable isotope ratio analysis. *Rapid Communications in Mass Spectrometry.* 15, 501-519.

WHO, 2000. Air quality guidelines for Europe. European Series. 2nd ed. World Health Organization, Copenhagen

Woolfenden, E., 2010a. Sorbent-based sampling methods for volatile and semi-volatile organic compounds in air. Part 1: Sorbent-based air monitoring options. *Journal of Chromatography A*.

Woolfenden, E., 2010b. Sorbent-based sampling methods for volatile and semi-volatile organic compounds in air. Part 2. Sorbent selection and other aspects of optimizing air monitoring methods. *Journal of Chromatography A.* 1217, 2685-2694.

Zoccolillo, L., Amendola, L., Cafaro, C., Insogna, S., 2005. Improved analysis of volatile halogenated hydrocarbons in water by purge-and-trap with gas chromatography and mass spectrometric detection. *Journal of Chromatography A.* 1077, 181-187.

Chapter 2

δD and $\delta^{13}C$ analyses of atmospheric volatile organic compounds by thermal desorption gas chromatography isotope ratio mass spectrometry

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Abstract

This paper describes the establishment of a robust method to determine compound specific δD and $\delta^{13}C$ values of volatile organic compounds (VOCs) in a standard mixture ranging between C_6 - C_{10} and was applied to various complex emission samples, e.g. from biomass combustion and car exhaust. A thermal desorption (TD) unit was linked to a gas chromatography isotope ratio mass spectrometer (GC-irMS) to enable compound specific isotope analysis (CSIA) of gaseous samples. TenaxTA was used as an adsorbent material in stainless steel TD tubes. We determined instrument settings to achieve a minimal water background level for reliable δD analysis and investigated the impact of storage time on δD and $\delta^{13}C$ values of collected VOCs (176 days and 40 days of storage, respectively). Most of the standard compounds investigated showed standard deviations (SD) < 6 ‰ (δD) when stored for 148 days at 4°C. However, benzene revealed occasionally D depleted values (21 ‰ SD) for unknown reasons. $\delta^{13}C$ analysis demonstrated that storage of 40 days had no effect on VOCs investigated. We also showed that breakthrough (benzene and toluene, 37 % and 7 %, respectively) had only a negligible effect (0.7 ‰ and 0.4 ‰, respectively) on $\delta^{13}C$ values of VOCs on the sample tube. We established that the sample portion collected at the split flow effluent of the TD unit can be used as a replicate sample for isotope analysis saving valuable sampling time and resources. We also applied TD-GC-irMS to different emission samples (biomass combustion, petrol and diesel car engines exhaust) and for the first time δD values of atmospheric VOCs in the above range are reported. Significant differences in δD of up to 130 ‰ were observed between VOCs in emissions from petrol car engine exhaust and biomass combustion (Karri tree). However, diesel car emissions showed a high content of highly complex unresolved mixtures thus a baseline separation of VOCs was not achieved for stable hydrogen isotope analysis. The ability to analyse δD by TD-GC-irMS complements the characterisation of atmospheric VOCs and is maybe used for establishing further source(s).

Keywords
volatile organic compounds; compound specific isotope analysis; BTEX; stable hydrogen isotopes; thermal desorption; active solid sorbent sampling

2.1 Introduction

Volatile organic compounds (VOCs) are ubiquitous in the environment (e.g. in soil, water and in the atmosphere) emitted by anthropogenic or natural sources. The technique of compound specific isotope analysis (CSIA) of organic compounds achieved by gas chromatography isotope ratio mass spectrometry (GC-irMS) has been often used in the fields of organic geochemistry, in food and in forensic investigations (including the provenance of food and drugs) (Meier-Augenstein, 1999; Klein-Breteler et al., 2002; Grice et al., 2007; Pilgrim et al., 2010). Techniques are currently available to measure $\delta^{13}C$ and δD of natural gas mixtures (e.g. methane to pentane), liquid hydrocarbons (e.g. crude oil) and extracts from complex media (e.g. soil, sediments and modern biological material) (Sun et al., 2003; de Groot, 2004; Dawson et al., 2005; Kinnaman et al., 2007). Thus, CSIA is useful to establish sources, processes, thermal history and fractionations that occur by kinetic and exchange reactions. The analysis of atmospheric VOCs was previously mainly restricted to $\delta^{13}C$ analysis (Rudolph et al., 2002; Goldstein and Shaw, 2003; Iannone et al., 2007; Giebel et al., 2010). A technique for measuring δD for a range of VOCs in emissions to establish their sources is not currently available. Therefore this study investigates a method to reliably measure the stable hydrogen isotope compositions of several VOCs without significant isotopic fractionation. We combined a successful established technique for collecting VOCs (thermal desorption) with traditional GC-irMS. Active solid sampling and thermal desorption (TD) in combination with TenaxTA as an adsorbent material are regularly used for sampling VOCs (Rothweiler et al., 1991; Dettmer and Engewald, 2002; Schneider and Goss, 2009). This sampling method has the advantages of (i) being selective for compounds of interest (C_6-C_{10}), (ii) its economical maintenance and (iii) the convenient sample handling in contrast to e.g. whole air sampling procedures (Rudolph et al., 1990). Previous studies could already demonstrate for stable

carbon isotope analysis that TD-GC-irMS is a reliable technique to analyse $\delta^{13}C$ of some low-molecular- weight VOCs (Turner et al., 2006; Peng et al., 2009).
We investigated the suitability of TD-GC-irMS for analysing δD in addition to expanding the range of VOCs (C_6-C_{10}) for $\delta^{13}C$ using TenaxTA as an adsorbent. Essential aspects of the technique were evaluated, e.g. influence of background water, sample breakthrough (BT) and storage behaviour. We also established that recollecting the split flow does not cause isotopic fractionation and thus can be used as a replicated sample for δD and $\delta^{13}C$ analyses. The application to various emissions (e.g. biomass combustion and car exhaust emissions) confirmed the robustness of TD-GC-irMS for stable isotope analysis.

2.2 Experimental Section

2.2.1 Chemicals, Materials and Gases

Standard mixtures contained VOCs ranging from C_6 – C_{10}. Compounds (benzene, toluene, ethylbenzene, styrene, *m*-xylene, *o*-xylene, *p*-xylene, *n*-propylbenzene, cumene, 1,2,4-trimethylbenzene, butylbenzene) were purchased from Sigma Aldrich and Fluka with purities ≥ 99.5 %. Standard mixtures were prepared gravimetrically in *n*-pentane (A.R.). *n*-Pentane was found to be the most suitable solvent for the analyses of investigated VOCs by GC-MS and GC-irMS. Five different standard concentrations were prepared for TD-GC-MS calibration (230 ng/µL, 170 ng/µL, 115 ng/µL and 34 ng/µL) from a stock solution of 340 ng/µL. For analyses by GC-irMS (i.e. without a TD unit) standard solutions of 250 ng/µL were used. For analyses by TD-GC-irMS solutions consisting of ca. 520 ng of each compound per µL were prepared.

Commercially available adsorbent materials for TD are suitable for a wide range of compounds and different fields of application (Dettmer and Engewald, 2002). For the present study we chose TenaxTA due to its highly hydrophobic characteristics and its selectivity for VOCs of interest (C_6 to C_{10}, boiling points between 80 °C and 220 °C). TenaxTA is a porous polymer resin on the basis of 2,6-diphenylene oxide and was purchased from Agilent Technologies in mesh 60/80.

In this paper we compared the chromatographic performance of the VOCs on two GC stationary phases (i) a polyethylene glycol (DB-WAXetr) and (ii) a non-polar phenyl-arylene polymer (DB5-MS). Both columns were supplied from Agilent J&W with dimensions of 60 m length x 0.25 mm i.d. and a 0.25 µm film thickness.

Reference gases (H_2 and CO_2) for stable isotope analyses were purchased from BOC Gases Australia Ltd. in ultra high purity (99.999 %).

2.2.2 Preparation of the TD tubes

Tubes were manually packed with approximately 280 mg of TenaxTA with minimal compression. Backpressure tests for each TD tube confirmed that packing was consistent (approximately -1.2 kPa). TenaxTA was conditioned at 330 °C (4 hours) while a constant flow of pure helium (50 mL/min) was passed through the tube.

Standard TD tubes were prepared in accordance to method TO-17 (US-EPA, 1999). An aliquot of 2 µL - 4 µL of the standard mix was injected directly onto the sorbent bed while pumping air through the tube for 1 min at 50 mL/min. It is important to note that the TD-tube needs to be positioned vertically during injection and sampling to avoid possible BT by channelling. Thus a BT experiment was also performed (see 2.3.5). A standard solution of high concentration (i.e. 800 ng per compound/µL) was injected (3 µL) onto a sample tube using a Calibration Solution Loading Rig (CSLR™) (Markes, 2006). The CSLR™ consisted of an unheated injector port with a controlled carrier gas supply (i.e. helium). The standard mix was introduced through the injector septum using a standard GC syringe. A helium flow of 200 mL/min was swept through the injection port for 40 min. The solution vaporised in the flow of gas before it reached the sorbent bed in the TD tube.

2.2.3 Collection of Emissions

Three different emissions were collected to investigate the applicability of TD-GC-irMS on real samples (biomass combustion, petrol and diesel car engine's exhaust). All samples were actively drawn through TenaxTA sample tubes using a compact Gilian LFS hand pump. Sampling volume was depending on the emission concentration to gain a sufficient amount of VOCs for stable isotope analysis. Sampling flow was adjusted accordingly but in the recommended range for active solid sampling (Harper, 2000; Woolfenden, 2010).

(i) For the petrol engine exhaust emissions samples were taken from a 1993 Mitsubishi Magna Executive running on unleaded petrol (ULP). A sampling volume of 500 mL per sampling tube was collected (at 50 mL/min).

(ii) For the diesel engine exhaust emissions samples were taken from a 2008 Toyota Land Cruiser GXL. A sampling volume of 3L per sampling tube was collected (at 200 mL/min).

(iii) For emission sampling from biomass combustion approximately 1kg of Karri biomass (*eucalyptus diversicolor*) was burnt in a 150 L drum with sufficient oxygen supply for a complete combustion. A sampling volume of 3 L per sampling tube was collected (at 200 mL/min).

2.2.4 Instrumentation

Compound specific δD and $\delta^{13}C$ analyses of atmospheric VOCs were achieved by linking two established techniques (i) thermal desorption (to collect and pre-concentrate the sample) and (ii) GC-irMS (to separate the compounds in the sample mixture and allowing accurate δD and $\delta^{13}C$ measurements).

In addition to isotope analysis conventional TD-GC-MS analysis was used for compound identification and for evaluation of most suitable GC settings.

2.2.4.1 Thermal Desorption (TD) Unit

The TD unit (UNITY2™, Markes International Limited) used was a single tube, two-stage desorber (primary sample tube desorber and cold trap desorber). The desorption oven was suitable for stainless steel sample tubes (0.635 cm O.D. and 8.89 cm length). The installed cold trap contained also the adsorbent material and was cooled by a 2-stage peltier cell to temperatures ranging between -10 °C and 30 °C. The first step of the analyses was the thermal desorption of the sample tube at 300 °C for 5 min at an adjustable but constant helium flow (**Table 2.1**). The desorbed compounds were trapped on the cold trap at 10°C. In a second step the refocused sample was rapidly desorbed from the cold trap at 100 °C/s to 300 °C and held for 1min. The sample was then transferred onto the GC-column through a heated deactivated fused-silica capillary (120°C) in the helium carrier gas (**Figure 2.1**). The instant desorption process focused the sample on the GC-column to improve the chromatographic resolution. The helium flow during trap desorption represents the sum of GC helium flow and split flow (when required) but needs a minimum flow of 2 mL/min for sufficient desorption. Prior to each sample desorption the TD unit performed an automated leak test and sample tube and cold trap were purged for 2 min and 1 min, respectively using helium to remove any residual oxygen. The purge flow used was equivalent to the desorption flow (**Table 2.1**).

Table 2.1: TD-unit flow settings for different tests

parameter	linearity test	storage test	split tube test δD	split tube test $\delta^{13}C$	BT test	concentration test
column flow	1 ml/min	0.9 ml/min	0.9 ml/min	1.1 ml/min	1.1 ml/min	1.1 ml/min
desorb flow	50 ml/min	45 ml/min	45 ml/min	15 ml/min	15 ml/min	10; 20 ml/min
split flow during **tube** desorb	10 ml/min	no split	45 ml/min	no split	no split	no split
split flow during **trap** desorb	10 ml/min	no split	no split	25 ml/min	2; 12 and 25 ml/min	80; 19 ml/min

During both desorption steps it was possible to divert a split flow from the sample flow as required depending on the sample concentration. The actual split ratio is achieved by adjusting the volume of the split flow. A special feature

offered by UNITY2TM is a device for quantitative re-collection of the split flow on a separate sample tube (SecureTD-Q) (**Figure 2.1**). Thus the split sample provides a replicate of the injected sample. Detailed information about general instrument operation of the UNITY2TM is provided by Bates et al. (Bates et al., 2008).

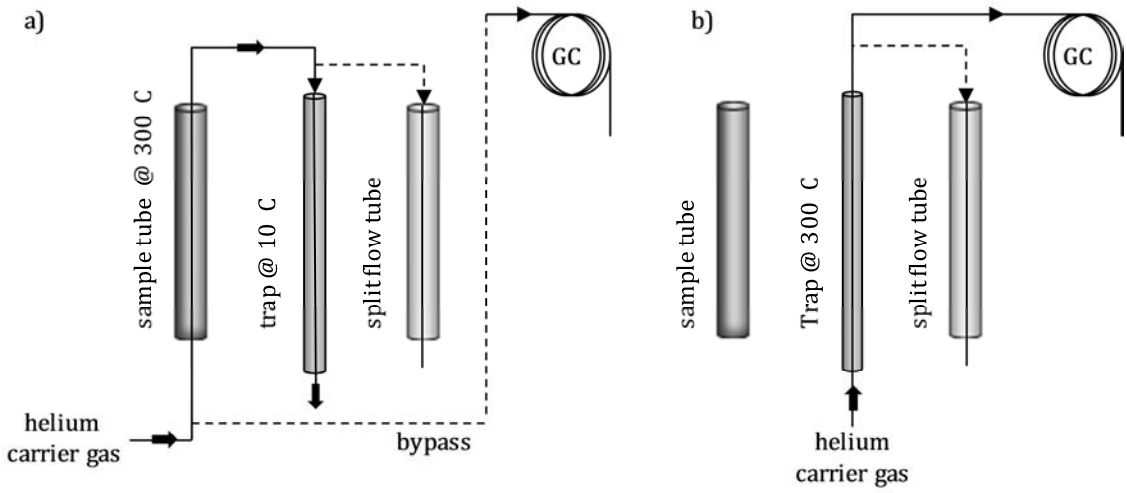

Figure 2.1: Sequences of TD operation a) sample tube desorption and b) cold trap desorption. An optional split flow is illustrated in a discontinuous line

2.2.4.2 Gas Chromatography - Mass Spectrometry (GC-MS)

The method development for TD-GC-MS analysis was carried out on an HP6890 GC linked to an HP5973 MS detector. The GC oven temperature was held isothermally at 50 °C for 5 min and heated at 5 °C/min to 80 °C, held for 5 min and heated again at 12 °C/min to a final temperature of 220 °C for 2 min. The GC had to be set to splitless and constant pressure mode (108.3 kPa). Peak identification was performed in scan mode using m/z between 18 and 200.

2.2.4.3 Gas Chromatography - isotope ratio Mass Spectrometry (GC-irMS)

CSIA was performed on a Micromass IsoPrime irMS interfaced with an HP6890 GC, programmed with the same temperature settings as described above for GC–MS analysis. An auto-sampler (HP6890) was used for direct injections of the sample mix (split/splitless injector) in pulsed-splitless mode. Isotopic compositions of sample components are given in the delta (δ) notation in per mil (‰) relative to the Vienna Standard Mean Ocean Water (VSMOW)

(hydrogen) or to the VPDB carbonate standard (carbon) (Equation 1). A reference gas pulse of a known D/H or $^{13}C/^{12}C$ content was introduced into the isotope mass spectrometer at a time different to the analyses. Stable isotopic ratios are reported relative to that of the reference gas which was determined daily using organic standards (with known δ values) to monitor the instrument's performance and reliability of the results.

$$\delta_{sample} = \left[\frac{R_{sample} - R_{standard}}{R_{standard}}\right] * 1000 \qquad \text{(Equ 2.1)}$$

R is the ratio of heavy to light isotope (D/H, $^{13}C/^{12}C$)

The basic principles of δD analysis are shown in **Figure 2.2** and relevant calculations are previously described elsewhere (Prosser and Scrimgeour, 1995; Burgøyne and Hayes, 1998; Dawson et al., 2004; Dawson et al., 2007). In brief, GC chromatographically separated compounds are pyrolysed at 1050 °C to H_2 +C +CO in a quartz furnace containing a sieved chromium catalyst. δD values were calculated by integrating the peaks of resulting ion currents of masses 2 and 3 (H_2 and HD). The results of the H^{3+} corrections (performed after Sessions et al. (2001)) were automatically included in software calculations.

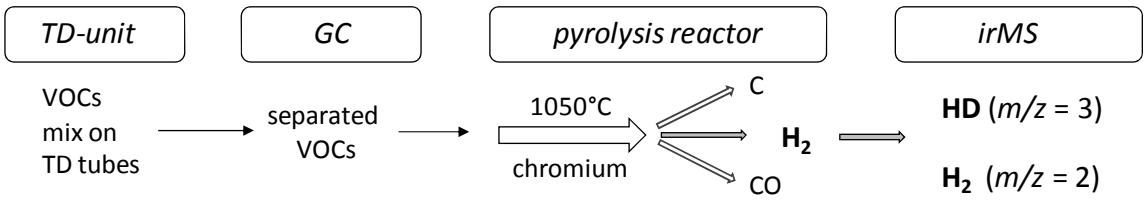

Figure 2.2: Principle of δD analysis by TD-GC-irMS

$\delta^{13}C$ values were calculated by integration of the masses 44, 45 and 46 ion currents of the peaks produced by combustion (CuO reactor at 850°C) of the chromatographically separated compounds to CO_2 +H_2O (**Figure 2.3**). The generated water was trapped at -100°C to avoid the interference of HCO_2^+ (*m/z* 45).

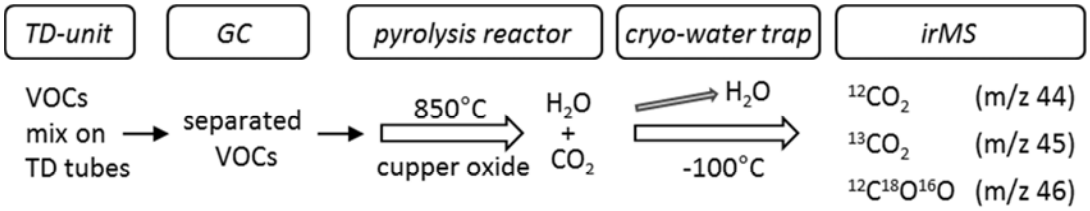

Figure 2.3: Principle of $\delta^{13}C$ analysis by TD-GC-irMS

For samples, average values of at least three analyses are reported and standard deviations (SD) are given. For direct injections an internal standard mix of five compounds (*n*-undecane, *n*-tridecane, *n*-tetradecane, *n*-heptadecane, *n*-octadecane, *n*-nonadecane, pentacosane) with known δD and $\delta^{13}C$ values was analysed after every 10^{th} sample to monitor accuracy and precision of δ measurements. During the measurements, SDs of the internal standard for analyses were typically less than 4 ‰ (δD) and less than 0.3 ‰ ($\delta^{13}C$).

2.3 Results and Discussion

2.3.1 Background Water

The impact of water on results obtained by TD and active solid sampling in its many forms were previously discussed (Helmig and Vierling, 1995; Woolfenden, 2010). However, most published data refer to a scan range above m/z 30 excluding the detection of water during measurements. The presence of water anywhere in the system will have an impact on δD analyses since pyrolysis will transfer water to hydrogen gas (H_2, DH). Therefore we monitored m/z ion 18 during TD-GC-MS preliminary tests on two different GC-columns (DB-5MS and DB-Waxetr) and noted an increased background and an additional peak in contrast to GC-MS analysis without TD unit. The mass spectrum indicated that the component was water. The occurrence of the peak and background elevation during D/H analysis using TD-GC-irMS verified the hydrogen content. Tests with packed (adsorbent without a sample) and empty (unpacked) TD tubes showed no difference of the background level. Efforts were made to minimise the water content by using a highly hydrophobic adsorbent material (TenaxTA) and following the TD unit's water restriction measures as well as applying standardised sampling methods (e.g. guidelines from U.S. EPA (1999)).

Thorough leak checks on the TD-unit and all connections to the GC were carried out and various instrument parameters were investigated. Despite these efforts, the elevated background level and peak due to water was still observed but we found that by using cold trap temperatures of 10 °C and by maintaining a split flow of > 1 mL/min during trap desorption the background water was significantly reduced (**Figure 2.4**) allowing accurate δD measurements (see 2.3.3). Additionally the determined GC oven temperatures (see 2.2.4.2) enabled the separation of toluene from the remaining water peak (**Figure 2.4b**).

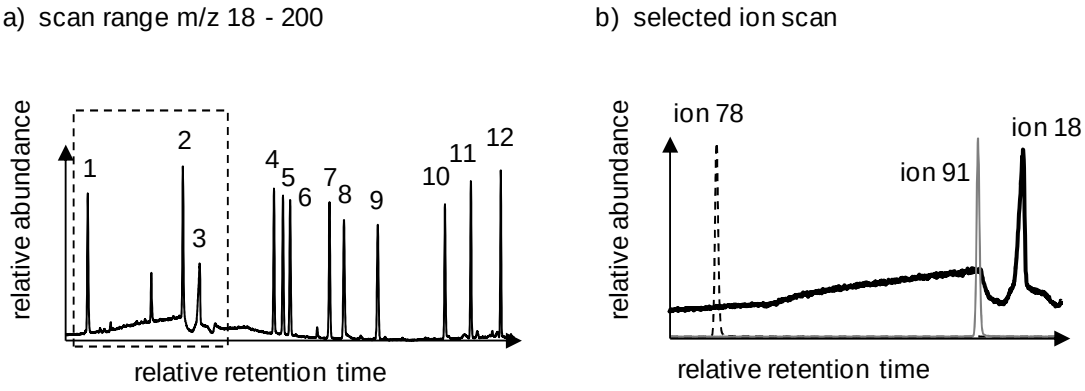

Figure 2.4: TD-GC-MS analysis of a standard mix a) from all compounds 1-benzene, 2-toluene, 3-water, 4-ethylbenzene, 5-*p*-xylene, 6-*m*-xylene, 7-cumene, 8-*o*-xylene, 9- *n*-propylbenzene, 10-styrene, 11-1,2,4-trimethylbenzene, 12-butylbenzene, respectively and b) its extracted ion chromatogram for ion 78 (benzene), 91 (toluene) and 18 (water).

2.3.2 Comparison of GC-columns

The performance of a DB-Waxetr and a DB-5MS GC column was investigated for VOCs of the standard mixture analysed by TD-GC-MS. The DB-5MS is known to be less prone to damage by oxygen and generally has less column-bleed compared to the DB-Waxetr column. The advantage of the DB-Waxetr column over the DB-5MS is its higher polarity and thus its ability to separate *p*- and *m*-xylene isomers. For this study the column bleed had negligible impact on the compounds investigated. Therefore the DB-Waxetr was chosen for further analysis due to the efficient separation of all compounds of interest.

2.3.3 Isotopic Fractionation

Previous work established that TD does not cause isotopic fractionation for $\delta^{13}C$ analysis of selected VOCs (C_2 – C_9) (Turner et al., 2006; Peng et al., 2009). In this study we investigated if any isotopic fractionation occurred for VOCs of the standard mixture during compound specific δD analysis using TD. Therefore results achieved by TD-GC-irMS were compared to those obtained by GC-irMS (direct injection) analyses. The specifications of the irMS required sample sizes of >250 ng per compound on the GC column to measure δD in the limits of instrument linearity. Due to the essential split flow setting of >1 mL/min during trap desorption (see water restriction measures in 2.3.1) samples in order >500 ng per compound needed to be collected on the adsorbent material. We could show repeatable results with SDs between 1-5 ‰ (average of 2‰). δD values of most investigated compounds introduced by TD are slightly heavier (on average 4 ‰) compared to δD values obtained by direct injection. However, the differences are still in range of instrument error (with the exception of 1,2,4-trimethylbenzene having an 11‰ difference between the two techniques) and therefore are deemed negligible. Thus we have shown that TD-GC-irMS is a reliable method for obtaining δD results of VOCs ranging between C_6-C_{10}.

2.3.4 Impact of Storage Time on δD and $\delta^{13}C$ of VOCs

The impact of storage time on δD and $\delta^{13}C$ values of VOCs was investigated for the VOCs in the standard mix adsorbed on TenaxTA. All desorption tubes were stored at 4 °C in an air tight jar containing activated charcoal. $\delta^{13}C$ results were determined after 8, 14, 16 and 40 days of storage and showed negligible differences (SD between 0.1 and 0.3 ‰) for all VOCs (**Table 2.2**)

Table 2.2: Results for $\delta^{13}C$ [‰] analyses of VOCs in the standard mixture for up to 40 days of storage.

time of storage [d]	**0**	**8**	**14**	**16**	**40**	*SD [‰]*
benzene	-26.7	-26.6	-26.6	-26.6	-26.7	*0.1*
toluene	-25.9	-25.8	-25.7	-25.6	-25.9	*0.1*
ethylbenzene	-28.4	-27.5	-28.2	-27.8	-28.1	*0.3*
p -xylene	-27.6	-27.4	-27.3	-27.4	-27.7	*0.2*
m -xylene	-27.0	-26.8	-26.7	-26.7	-27.1	*0.2*
cumene	-26.5	-27.0	-26.4	-26.4	-26.3	*0.3*
o -xylene	-29.7	-29.8	-29.7	-29.7	-30.1	*0.2*
n -propylbenzene	-28.5	-28.3	-28.9	-28.6	-29.0	*0.3*
styrene	-28.4	-28.5	-28.2	-28.0	-28.1	*0.2*
1,2,4-trimethylbenzen	-26.5	-26.5	-26.6	-26.5	-26.8	*0.1*
butylbenzene	-25.1	-24.9	-25.3	-25.1	-25.5	*0.2*

δD values were obtained during 176 days of storage (i.e. after 2, 4, 8, 24, 32, 50, 72, 240 hours and after 148 and 176 days) (**Table 2.3**). SDs of δD analyses were negligible for most compounds of the standard mixture ranging between 3 – 6 ‰ during the first 148 days of storage. However, results obtained after 176 days of storage showed generally more depleted δD values of up to 44 ‰ compared to δD values obtained on day 0. The acquired δD values of benzene showed dissimilarities to other VOCs during the first 146 days of storage with a SD of 21 ‰ although the majority of benzene's δD values vary less than 3 ‰ to the reference δD value (day 0). The variations in benzene's δD values show no clear trend with storage time (**Table 2.3**), however, a random volatility effect cannot be excluded (Wang and Huang, 2003) possibly due to the lowest boiling point among the VOCs of the standard mixture. Benzene could have been also subjected to hydrogen exchange with a depleted hydrogen source. Although the exact cause is unclear; therefore it is suggested to use multiple sampling tubes for real samples to identify occasional shifts in δD values for benzene during storage.

Table 2.3: Results for δD [‰] analyses of VOCs (standard mixture) for up to 176 days of storage; mean δD ± SD [‰] over 146 days; shift in δD between day 0 to day 176

time of storage [h]	**0**	**2**	**4**	**8**	**24**	**32**	**50**	**72**	**240**	**3552**	**mean ± SD**	**4224**	**$\Delta_{0\text{-}176}$**
time of storage [d]	**0**	**0.1**	**0.2**	**0.3**	**1.0**	**1.3**	**2.1**	**3.0**	**10**	**148**		**176**	
benzene	-86	-85	-107	-84	-85	-89	-129	-128	-133	-87	-101 ± 21	-98	12
toluene	-58	-67	-53	-64	-64	-66	-57	-53	-61	-62	-61 ± 5	-102	44
ethylbenzene	-41	-33	-30	-30	-31	-32	-31	-30	-31	-47	-34 ± 6	-80	38
p -xylene	-60	-55	-52	-53	-52	-54	-53	-53	-52	-61	-55 ± 3	-53	-7
m -xylene	-85	-86	-83	-84	-81	-85	-84	-85	-84	-91	-85 ± 3	-106	20
cumene	-47	-44	-41	-44	-43	-44	-44	-42	-45	-54	-45 ± 4	-50	3
o -xylene	-146	-144	-143	-149	-143	-149	-149	-143	-150	-156	-147 ± 4	-149	2
n -propylbenzene	-88	-87	-85	-88	-85	-88	-88	-79	-89	-92	-87 ± 3	-96	9
styrene	-52	-47	-45	-46	-49	-48	-49	-50	-47	-55	-49 ± 3	-71	19
1,2,4-trimethylbenzene	-100	-103	-100	-104	-102	-102	-104	-98	-102	-111	-103 ± 3	-112	12
butylbenzene	-20	-20	-22	-26	-22	-23	-26	-24	-19	-20	-22 ± 3	-37	17

2.3.5 Effects of Breakthrough

BT can occur during active solid sampling due to specific sampling conditions or the nature of the real sample (Peters and Bakkeren, 1994). Therefore it is important to monitor any possible BT by installing a BT tube just after the sample tube. We evaluated whether any carbon isotopic fractionation occurred during BT by analysing the standard mixture. An aliquot of the standard (3 µL) was introduced onto the sampling tube using a CSLR™. The sampling tube and BT tube were linked with a brass connector and purged with a helium flow of 200 mL/min (40 min) to allow for BT of benzene and toluene based on parameters from the Health and Safety Executive regulations, UK (HSE, 1993). We found that 37 % of benzene and 7 % of toluene broke through. Other compounds in the standard mix did not show any significant BT. **Figure 2.5** illustrates the $\delta^{13}C$ values of benzene and toluene obtained from the sample tube, from the BT tube and from a reference analysis by TD-GC-irMS during standard injection. The δ values from the BT tube were less depleted in ^{13}C by 1.6 ‰ (benzene) and 3.3 ‰ (toluene) compared to those from the sample tube. However, comparing the results from sample tubes where BT occurred to those without BT $\delta^{13}C$ values showed no significant differences (0.7 ‰ and 0.4 ‰ for benzene and toluene, respectively) (**Figure 2.5**). Therefore the impact of BT of benzene and toluene on their $\delta^{13}C$ is negligible. The effect of BT on δD values for benzene and toluene was not investigated. It is assumed that BT of benzene and toluene would have also only a minimal effect on their δD values since stable isotopes of C and H have similar physical properties in this regard.

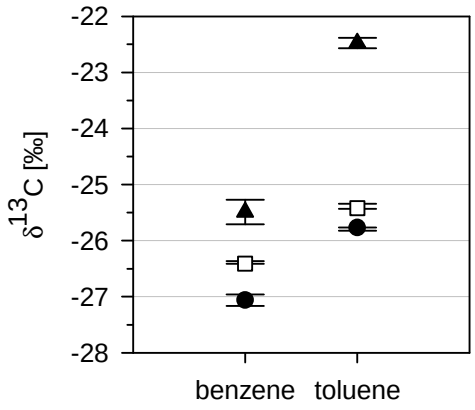

Figure 2.5: $\delta^{13}C$ values of benzene and toluene in the standard mix collected on a (•) sample tube and on the subsequent (▲) breakthrough tube compared to a $\delta^{13}C$ value of a (❑) reference analysis (adsorption without breakthrough)

2.3.6 Usage of the Split Flow Sample

Having the opportunity to obtain a replicate sample from the split flow presents several advantages over traditional TD-units. These include (i) obtaining a duplicate sample allowing TD-GC-irMS measurements at different concentrations of the same sample, which is achieved by varying the split ratio of the TD unit (The merit of the split flow collection is demonstrated in its application to emission samples, see 2.3.7.) (ii) obtaining required replicate δ values, (iii) obtaining a duplicate sample for identifying compounds by TD-GC-MS which leads to (iv) saving important sampling time and resources. It reduces significantly the number of samples to be taken in the field without compromising the need for replicate analyses.

The δD results obtained for VOCs from the split flow tube were similar/ identical to those obtained on the sample tube (**Figure 2.6**). This is supported by results from multiple sample collection of the split flow effluent (circle of 6 split flow collections) with SD < 0.2 ‰ ($\delta^{13}C$).

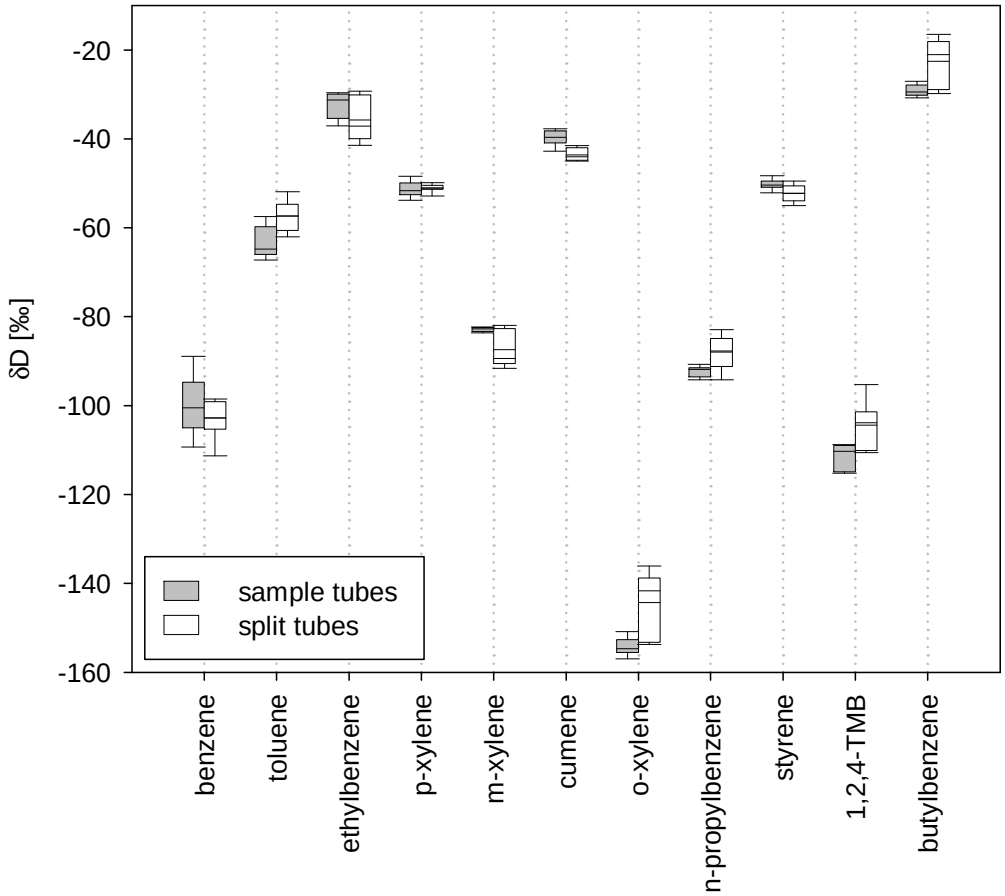

Figure 2.6: Differences between δD values of VOCs in the standard mix on the sample tube and on the associated split flow tube. (TMB = trimethylbenzene)

2.3.7 δD Analyses of VOCs in Different Emissions

δD analysis by TD-GC-irMS was applied to three emission sources (biomass combustion, petrol and diesel car engines). **Table 2.4** shows the δD values of collected VOCs. Most SDs for δD analyses of VOC in the emissions from a petrol engine and biomass combustion range between 1 and 5 ‰ and are well within the instrument precision. However, SDs are up to 14 ‰ for analyses of VOCs from the diesel engine emissions which is related to a highly complex unresolved mixture of compounds. For CSIA it is essential to obtain baseline separation for compounds of interest. This was not the case for the diesel sample.

To obtain reliable δD values for an array of compounds samples needed to be analysed at different concentrations (different split ratios) in order to assess the data within the linear range of the instrument by using the replicate samples of the split flow collection. The comparison of δD values of benzene, toluene and *m*-xylene (**Table 2.4**) demonstrate significant differences (27 ‰, 37 ‰ and 130 ‰, respectively) between emissions from a petrol car engine and from biomass combustion (Karri). Thus clear source differentiation carries the potential to be used in source tracking of VOCs.

Table 2.4: δD values [‰] of VOCs in car exhaust emissions (petrol and diesel engine) and in biomass combustion emissions (Karri - *Eucalyptus diversicolor)* with related standard deviations (SD) [‰]; n = number of analyses; δ_K = δD values Karri; δ_p = δD values petrol engine

	diesl car exhaust emission		**petrol car exhaust emission**		**Karri combustion emission**		
compound	**δD ± SD**		**δD ± SD**		**δD ± SD**		**Δ δ_K - δ_p**
benzene	10 ± 9	n=4	-94 ± 5	n=5	-121 ± 5	n=3	27
toluene	-3 ± 8	n=6	-65 ± 3	n=6	-102 ± 6	n=3	37
ethylbenzene			-47 ± 4	n=3			
p -xylene			-44 ± 3	n=3			
m -xylene	-70 ± 14	n=5	-61 ± 3	n=5	-191 ± 5	n=3	130
o -xylene	-49 ± 12	n=3	-48 ± 4	n=3			
limonene					-242 ± 2	n=3	
eucalyptol					-279 ± 5	n=3	
styrene					-113 ± 2	n=3	
trimethylbenzene	-117 ± 14	n=5	-43 ± 5	n=3			
naphthalene	-65 ± 4	n=6			-102 ± 1	n=3	

2.4 Conclusions

In this study we investigated compound specific δD and $\delta^{13}C$ analysis using thermal desorption to collect and concentrate atmospheric VOCs (C_6 – C_{10}) using TenaxTA as adsorbent material. We established a reliable method enabling reproducible results for δD and $\delta^{13}C$ analyses with negligible isotopic fractionation compared to direct standard analyses. We evaluated the impact of storage time on δD and $\delta^{13}C$ values and revealed that BT has only minor impact on δ values. We also showed that the sample portion collected of the split flow effluent can be used as a replicate sample for isotope analysis saving valuable sampling time and recourses.

This paper presents for the first time δD values of VOCs in emission samples showing a clear distinctions of δD between emissions from biomass combustion and car exhaust emissions (petroleum engine). TD-GC-irMS is a reliable technique and maybe used for establishing further source(s).

Acknowledgements

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2.5 References

Bates, M., Bruno, P., Caputi, M., Caselli, M., De Gennaro, G., Tutino, M., 2008. Analysis of polycyclic aromatic hydrocarbons (PAHs) in airborne particles by direct sample introduction thermal desorption GC/MS. *Atmospheric Environment* 42, 6144-6151.

Burgøyne, T., Hayes, J., 1998. Quantitative production of H_2 by pyrolysis of gas chromatographic effluents. *Analytical Chemistry* 70, 5136-5141.

Dawson, D., Grice, K., Alexander, R., 2005. Effect of maturation on the indigenous δD signatures of individual hydrocarbons in sediments and crude oils from the Perth Basin (Western Australia). *Organic Geochemistry* 36, 95-104.

Dawson, D., Grice, K., Alexander, R., Edwards, D., 2007. The effect of source and maturity on the stable isotopic compositions of individual hydrocarbons in sediments and crude oils from the Vulcan Sub-basin, Timor Sea, Northern Australia. *Organic Geochemistry* 38, 1015-1038.

Dawson, D., Grice, K., Wang, S., Alexander, R., Radke, J., 2004. Stable hydrogen isotopic composition of hydrocarbons in torbanites (Late Carboniferous to Late Permian) deposited under various climatic conditions. *Organic Geochemistry* 35, 189-197.

de Groot, P.A., 2004. Handbook of Stable Isotope Analytical Techniques. Elsevier Science, Ham, Belgium.

Dettmer, K., Engewald, W., 2002. Adsorbent materials commonly used in air analysis for adsorptive enrichment and thermal desorption of volatile organic compounds. *Analytical and Bioanalytical Chemistry* 373, 490-500.

Giebel, B., Swart, P., Riemer, D., 2010. $\delta^{13}C$ stable isotope analysis of atmospheric oxygenated volatile organic compounds by gas chromatography-isotope ratio mass spectrometry. *Analytical Chemistry* 82, 6797–6806.

Goldstein, A., Shaw, S., 2003. Isotopes of volatile organic compounds: An emerging approach for studying atmospheric budgets and chemistry. *Chemical Reviews* 103, 5025-5048.

Grice, K., Nabbefeld, B., Maslen, E., 2007. Source and significance of selected polycyclic aromatic hydrocarbons in sediments (Hovea-3 well, Perth Basin, Western Australia) spanning the Permian-Triassic boundary. *Organic Geochemistry* 38, 1795-1803.

Harper, M., 2000. Sorbent trapping of volatile organic compounds from air. *Journal of Chromatography A* 885, 129-151.

Helmig, D., Vierling, L., 1995. Water adsorption capacity of the solid adsorbents Tenax TA, Tenax GR, Carbotrap, Carbotrap C, Carbosieve SIII, and Carboxen 569 and water management techniques for the atmospheric sampling of volatile organic trace gases. *Analytical Chemistry* 67, 4380-4386.

HSE, 1993. Volatile organic compounds in air. MDHS 72, Health and Safety Laboratory, Norwich, UK

Iannone, R., Koppmann, R., Rudolph, J., 2007. A technique for atmospheric measurements of stable carbon isotope ratios of isoprene, methacrolein, and methyl vinyl ketone. *Journal of Atmospheric Chemistry* 58, 181-202.

Kinnaman, F., Valentine, D., Tyler, S., 2007. Carbon and hydrogen isotope fractionation associated with the aerobic microbial oxidation of methane, ethane, propane and butane. *Geochimica et Cosmochimica Acta* 71, 271-283.

Klein-Breteler, W., Grice, K., Schouten, S., Kloosterhuis, H.T., Damste, J.S.S., 2002. Stable carbon isotope fractionation in the marine copepod *Temora longicornis*: unexpectedly low $\delta^{13}C$ value of faecal pellets. *Marine Ecology Progress Series* 240, 195-204.

Markes, 2006. Calibration: Preparing and introducing thermal desorption standards using sorbent tubes. TDTS-07, Markes International Limited Llantrisant, UK

Meier-Augenstein, W., 1999. Applied gas chromatography coupled to isotope ratio mass spectrometry. *Journal of Chromatography A* 842, 351-371.

Peng, L., Zhang, H., Ren, Z., Mu, L., Shi, R., Chang, L., Li, F., 2009. The carbon isotopic compositions of non-methane hydrocarbons in atmosphere. *Chinese Science Bulletin* 54, 1422-1425.

Peters, R., Bakkeren, H., 1994. Sorbents in sampling. Stability and breakthrough measurements. *The Analyst*.

Pilgrim, T.S., Watling, R.J., Grice, K., 2010. Application of trace element and stable isotope signatures to determine the provenance of tea (*Camellia sinensis*) samples. *Food Chemistry* 118, 921-926.

Prosser, S.J., Scrimgeour, C.M., 1995. High-precision determination of $^{2}H/^{1}H$ in H_2 and H_20 by continuous-flow isotope ratio mass spectrometry. *Analytical Chemistry* 67, 1992-1997.

Rothweiler, H., Wäger, P., Schlatter, C., 1991. Comparison of Tenax TA and Carbotrap for sampling and analysis of volatile organic compounds in air. *Atmospheric Environment. Part B. Urban Atmosphere* 25, 231-235.

Rudolph, J., Czuba, E., Norman, A., Huang, L., Ernst, D., 2002. Stable carbon isotope composition of nonmethane hydrocarbons in emissions from transportation related sources and atmospheric observations in an urban atmosphere. *Atmospheric Environment* 36, 1173-1181.

Rudolph, J., Müller, K., Koppmann, R., 1990. Sampling of organic volatiles in the atmosphere at moderate and low pollution levels. *Analytica Chimica Acta* 236, 197-211.

Schneider, M., Goss, K., 2009. Systematic Investigation of the Sorption Properties of Tenax TA, Chromosorb 106, Porapak N, and Carbopak F. *Analytical Chemistry* 81, 3017-3021.

Sessions, A., Burgoyne, T., Hayes, J., 2001. Correction of H_3^+ contributions in hydrogen isotope ratio monitoring mass spectrometry. *Analytical Chemistry* 73, 192-199.

Sun, C., Cooper, M., Snape, C.E., 2003. Use of compound-specific $\delta^{13}C$ and δD stable isotope measurements as an aid in the source apportionment of polyaromatic hydrocarbons. *Rapid Communications in Mass Spectrometry* 17, 2611-2613.

Turner, N., Jones, M., Grice, K., Dawson, D., Ioppolo-Armanios, M., Fisher, S., 2006. $\delta^{13}C$ of volatile organic compounds (VOCs) in airborne samples by thermal desorption-gas chromatography-isotope ratio-mass spectrometry (TD-GC-irMS). *Atmospheric Environment* 40, 3381-3388.

US-EPA, 1999. Determination of volatile organic compounds in ambient air using active sampling onto sorbent tubes (Method TO-17). U.S. Environmental Protection Agency (EPA), Cincinnati, U.S.

Wang, Y., Huang, Y., 2003. Hydrogen isotopic fractionation of petroleum hydrocarbons during vaporization: implications for assessing artificial and natural remediation of petroleum contamination. *Applied Geochemistry* 18, 1641-1651.

Woolfenden, E., 2010. Sorbent-based sampling methods for volatile and semi-volatile organic compounds in air. Part 2. Sorbent selection and other aspects of optimizing air monitoring methods. *Journal of Chromatography A* 1217, 2685-2694.

Chapter 3

$\delta^{13}C$ and δD of volatile organic compounds in an alumina industry stack emission

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Abstract

Compound specific isotope analysis (CSIA) is becoming more widely accepted as a tool for determining the sources of contaminants and monitoring their transport and fate in the environment. However, measuring δD of volatile organic compounds (VOCs) in atmospheric samples is still underexplored. The present study applies thermal desorption gas chromatography – isotope ratio mass spectrometry (TD-GC-irMS) for the first time to stable hydrogen isotope analyses of VOCs in an alumina refinery emission. $\delta^{13}C$ data is also collected. A sampling train was designed using TenaxTA as the adsorbent material to gain reliable and reproducible results for CSIA. $\delta^{13}C$ values for VOCs (C_6 to C_{14}) ranged from -22 to -31 ‰, which is similar to $\delta^{13}C$ value range reported for naturally occurring components. The δD values (21 to -137 ‰) in this study were consistently more enriched in D compared to δD values of VOCs previously reported making the δ values of VOCs in the industrial stack unique. Therefore δD analysis may provide a means for tracking VOCs in atmospheric samples.

Keywords

Compound specific isotope analysis; volatile organic compounds; stable hydrogen isotope analysis; stable carbon isotope analysis; thermal desorption

3.1 Introduction

Environmentally important compounds such as volatile organic compounds (VOCs) (WHO, 2000) or polycyclic aromatic hydrocarbons (Nelson et al., 2008) are derived from many different sources (Piccot et al., 1992; Kansal, 2009). Thermal degradation of any sort of material containing hydrocarbons causes the formation of VOCs depending on temperature and oxygen levels (see (Harrison and Hester, 1995) for more details). The US.EPA report of air quality in the US showed a significant reduction of vehicle related VOCs emission from 47 % to 27% in the last 10 to 20 years (US-EPA, 2000). This leaves the industry with 46 % as one of the main emitter of VOCs from anthropogenic sources (excluding wildfires and prescribed burns). Different approaches have been previously employed to trace the origin of atmospheric contaminants and to get

a better understanding of the contribution of the principal VOC emission sources to ambient concentrations. Using the relative abundance of components in a sample allows only rudimentary source identification for VOCs in ambient samples (Zalel et al., 2008) unless a large number of samples are analysed (Choi et al., 2010). A more promising method is compound specific isotope analysis (CSIA). This technique has allowed geochemists to establish the source of natural occurring compounds in complex mixtures such as petroleum and sediment extracts (Grice and Brocks, 2011). CSIA has been increasingly used to track the source of contaminants, for example in soil and water (Slater, 2003; Schmidt et al., 2004; O'Sullivan and Kalin, 2008). Studies in these areas demonstrated that applying isotope ratios of more than one element is an effective approach to clearly characterise the source (Philp et al., 2002; Sun et al., 2003; Mancini et al., 2008; Pilgrim et al., 2010). Stable isotope analysis of atmospheric samples remains mainly limited to $\delta^{13}C$ analyses, e.g. for PAHs collected on particle filters (Okuda et al., 2002; Liu et al., 2005; Zhang et al., 2009). Only recently a few studies applied δD analysis to air samples, e.g. Rice and Quay (2009) investigated formaldehyde and Brass and Rockmann (2010) analysed CH4. Yamada et al. (2003) reported $\delta^{13}C$ and δD of n-alkanes in aerosols collected on pre-combusted quartz filters. CSIA specifically of airborne VOCs started in 1997 (Rudolph et al., 1997). Goldstein and Shaw (2003) gave an excellent review about isotope analysis of VOCs. Very recently Vitzthum von Eckstaedt et al. (2011a) extended the work of Turner et al. (2006) and showed that thermal desorption - gas chromatography – isotope ratio mass spectrometry (TD-GC-irMS) is also a reliable technique to measure D/H ratios of VOCs in emissions. A combination of $\delta^{13}C$ and δD values of atmospheric VOCs from an industry related source has never been attempted nor reported before.

In this paper we have applied TD-GC-irMS to measure $\delta^{13}C$ and δD of VOCs (C_6-C_{14}) from an industry stack emission. We have designed a device for multiple thermal desorption (TD) tubes to collect samples for reliable and reproducible measurements. Samples were taken from calcination emissions at an alumina refinery in Western Australia. To produce pure alumina from bauxite ore (Bayer process) calcination is the third step after extraction and precipitation, where aluminium hydroxide crystals are washed, dried and then heated to

approximately 1000°C to convert aluminium hydroxide to alumina. Bauxite deposits may contain up to 0.30 % of organic impurities which is the main source of organic compounds in emissions from the alumina refinery (CSIRO, 2004).

3.2 Experimental Section

3.2.1 Technique Selection

Active solid sampling (drawing air through a stainless steel TD tube containing an adsorbent material) was chosen in this study because (i) it was proven in an earlier study to be a reliable method for $\delta^{13}C$ and δD analyses of VOCs (Vitzthum von Eckstaedt et al., 2011a) (ii) the ease of handling and (iii) is less labour intensive in comparison to canister sampling, (iv) selective for a limited range of compounds (low-molecular-weight VOCs) for successful CSIA and (v) cost effective. This sampling technique operates by pumping a known volume of air through a TD tube to adsorb the VOCs passing through. The TD tube containing the adsorbed VOCs was inserted into a TD unit (Markes International Ltd.) and thermally desorbed and transferred to a GC using a flow of an inert carrier gas (helium) (see 3.2.5).

TenaxTA was chosen as the most suitable resin for the adsorption of VOCs of interest (Zielinska et al., 1996; Clément et al., 2000; Ribes et al., 2007). Its hydrophobic characteristics were critical to reduce the impact of moisture, especially when measuring δD of VOCs.

3.2.2 Reagents and Materials

A standard mix containing 11 VOCs ranging from C_6-C_{10} (benzene, toluene, ethylbenzene, *p*-xylene, *m*-xylene, cumene, *o*-xylene, *n*-propylbenzene, styrene, 1,2,4-trimethylbenzene, butylbenzene, naphthalene solved in *n*-pentane) were analysed to establish the reliability of the instrumental set up. Standards were analysed once a day using the same technique described in Vitzthum von Eckstaedt et al. (2011a). TD tubes were packed manually with approximately

280 mg of TenaxTA in a mesh size 60/80 with minimal compression. All tubes were thermally conditioned for 4 hours at 330°C prior to their first use and for 30 min at 310°C prior to every sampling event.

3.2.3 Sampling Train Design

The sampling set up described in this paper was designed for parallel sampling (**Figure 3.1**). It consisted of 6 pairs of TD tubes (sampling tube and subsequent breakthrough tube) to get a representative number of samples in a minimal time frame and to monitor possible breakthrough (BT). All material upstream of the sampling tubes (T-pieces, elbows, tubing and connectors) was made of inert polytetrafluoroethylene (PTFE) except the sampling probe which was made of glass (length of 60 cm). The sampling train consisted of two acrylic manifolds. Each manifold was equipped with three sample ports fitted with needle valves to act as mass flow controllers. The sampling ports consisted of brass nuts with Teflon ferrules for easy attachment to the sample tubes. Every sample tube had a subsequent BT tube where one BT tube per manifold was used for analyses. Those two BT tubes did not have the same position on the 2 manifolds to ensure successful sampling in the event of leakage or blockage in one stream. Sampling and BT tubes were coupled with brass unions with Teflon ferrules. Both manifolds were joined downstream with a plastic T-piece to the pump tubing. A rotameter and the back pressure gauge followed to indicate correct sampling or possible leaks or blockages. The rotameter scale reading was between 0-4 L/min and the back pressure gauge scale ranged between 0-(-100) kPa. The pump (model miniport by KNF Neuberger) was working at a constant flow of 6 L/min and was positioned at the end of the sample train. Flow through the sample tubes was adjusted by altering the amount of make-up gas using a fine metering valve on the make-up gas line (low pressure S series metering valve by Swagelok). For this work the make-up gas flow was set to its maximum flow to maintain a sampling flow of 1.2 L/min through the sampling train.

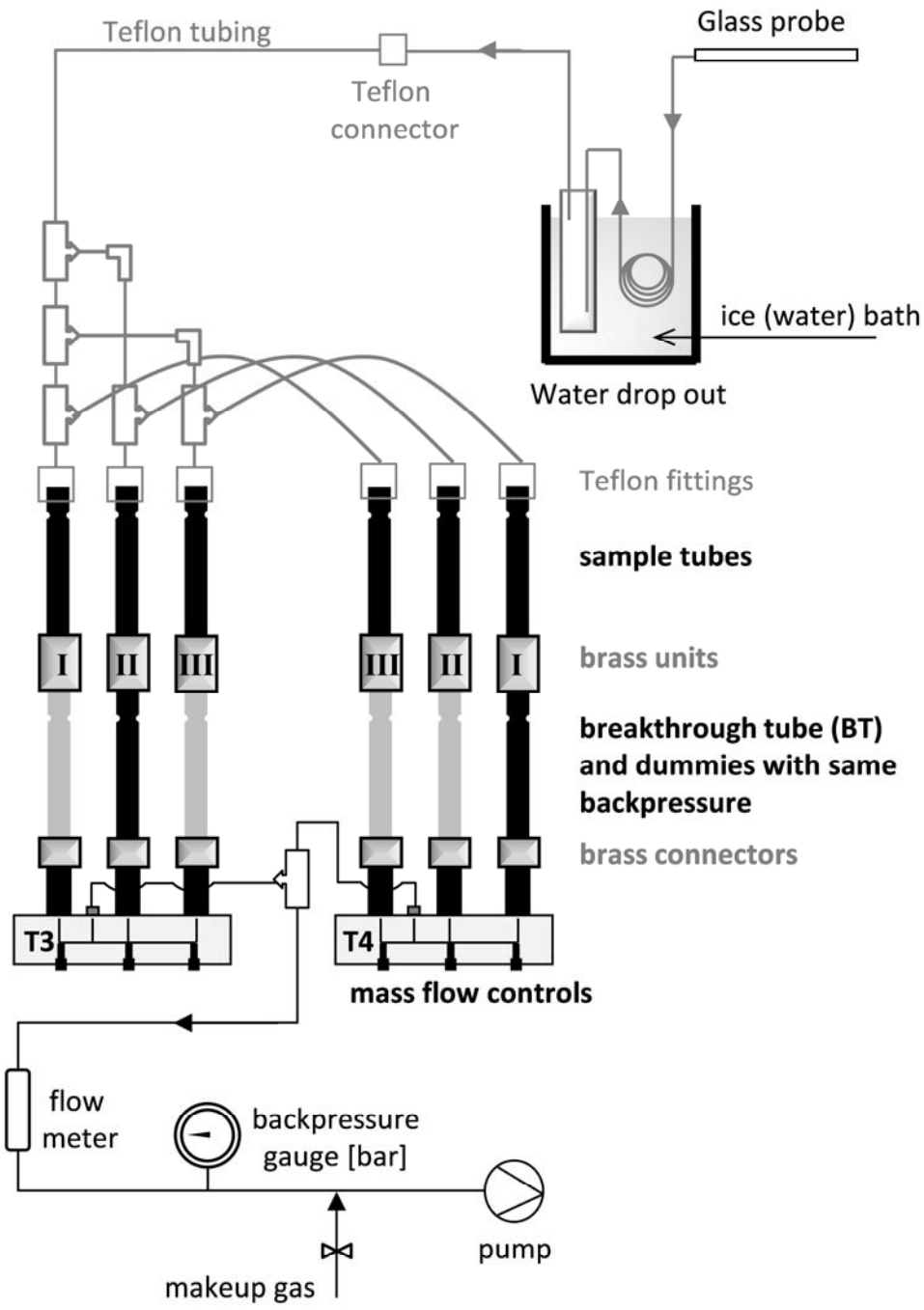

Figure 3.1: Schematic of the sampling set up

Mass flow controls on each stream line of the acrylic manifold were adjusted separately to provide equal flow rates measured with a digital flow meter (up-stream). The soap-bubble flow meter was connected after the pump to calibrate the reading of the digital flow meter. Similar back pressure of all TD tubes assured consistent flow rates through every stream line. Preliminary tests had shown that particulates were not an issue during sampling at the industry stack

and mechanical degradation of the TenaxTA absorbent was not detected in a significant quantity since the back pressures of the TD tubes remained consistent during sampling. The sample distribution was tested by connecting the sampling train to a calibration solution loading rig (CSLR™). An aliquot of the standard mix (3 µL) was vaporised into a helium flow of 50 mL/min per TD tube. During sampling it was vital to keep the TD tubes in an upright position to avoid channelling through the adsorbent material which could cause major BT.

3.2.4 Sampling Conditions

The sampling set up was placed on a platform at half the height of the stack at approximately 30 m above ground. The sampling probe was inserted horizontally into the stack (ca. 42 cm) perpendicular to the stack emission flow. The average total gas flow in the stack was 8700 m^3/h and the temperature was monitored at 150°C. As an approximate rule, retention volumes are reduced by 50% for every 10°C rise in temperature starting at 40°C (US-EPA, 1999; Kroupa et al., 2004; Woolfenden, 2010). Therefore the sampling probe was connected to a water drop out bottle placed in a container filled with ice water. Removing the generated condensate of the gas stream before reaching the sampling tubes is critical. Trapping the water on the TD tubes could compromise the δD results significantly due to the production of H_2.

Emission samples were taken at a flow rate of 1.2 L/min which was constantly checked using a rotameter. The back pressure reading was always taken at the beginning and at the end of a sampling run. During each event the back pressure remained stable at -17 kPa (no particle filter in use). The weather conditions were constant on all sampling events (dry, partly cloudy) at ambient temperatures ranging between 14°C and 23°C. The sampling train was located in a shaded area or covered with aluminium foil to avoid spot heating. All TD tubes were transported and stored in a cooled air tight jar containing activated charcoal. A series of procedure blanks ensured transport integrity. The impact of the assembling and disassembling process (8 to 13 min) was monitored by mimicking this process at the sampling location using blank TD tubes.

Approximate sampling volumes were calculated for each compound on the basis of stack emission concentrations measured in 2002 (Coffey et al., 2002) to collect the required concentrations on the TD sampling tubes for CSIA (400 ng and 700 ng for $\delta^{13}C$ and δD analyses, respectively). Therefore a set of three different sampling volumes (6.8 L, 39 L and 104 L per tube) were chosen thus each sample volume targeted different VOCs according to their concentration in the emission.

3.2.5 Instrumentation

3.2.5.1 Thermal Desorption – Gas Chromatography - Mass Spectrometry

For TD-GC-MS analyses a TD unit (Unity2, Markes International Ltd.) was connected to an HP6890 GC linked to an HP5973 MS detector. Parameters were adapted from Vitzthum von Eckstaedt et al. (2011a) with slight modifications to the GC oven temperature settings. The oven temperature was programmed at 35°C for 5 min to 80°C at 5°C/min and isothermally held for 5 min, ramped again at 12°C/min to a final temperature of 240°C and held for 3 min. The analysis was performed under a constant pressure of 121.4 kPa to achieve an initial column flow rate of 1.1 mL/min. The mass spectrometer was operating at the scan range from *m/z* 18 to 200 to also monitor the moisture content. Samples were analysed on an Agilent J&W DB-WAXetr column (polyethylene glycol) with the dimensions of 60 m length x 0.25 mm i.d. with a 0.25 µm film thickness. The TD transfer line was held at 120°C. The primary desorption was set for 5 min at 300°C with a desorption flow of 15 mL/min (procedure blanks and BT tubes) and > 25 mL/min (sample tubes). The subsequent cold trap desorption was set for 1 min at 300°C with a flow of 1 mL/min (procedure blanks) and > 25 mL/min (BT and sample tubes).

3.2.5.2 Thermal Desorption – Isotope Ratio Gas Chromatography - Mass Spectrometry

TD and GC parameters were used as described above for TD-GC-MS analysis, with the exception of the GC head pressure (140.7 kPa maintaining an initial helium flow of 1.1 mL/min at 35°C) and the cold trap desorption flow. The latter comprised the sum of GC column flow and an optional split flow, depending on the sample/compound concentration. CSIA for carbon and hydrogen were performed on a Micromass IsoPrime continuous flow isotope ratio mass spectrometer similar to the system described by Hall et al. (1999). Isotopic compositions of sample components were given in the delta notation in per mil (‰) relative to Vienna Standard Mean Ocean Water (VSMOW) (hydrogen) or to the Vienna Pee Dee Belemnite (VPDB) (carbon) standard. The $\delta^{13}C$ data were obtained by integrating the ion currents for masses 44, 45 and 46 from the CO_2 produced by oxidation of each chromatographically separated component after passing through a quartz furnace packed with copper oxide pellets heated at 850°C. The δD values were calculated by integration of the ion currents for the masses 2 and 3 of the H_2 peaks produced by pyrolysis of the chromatographic separated compounds using a chromium catalyst at 1050°C. The compositions were reported relative to that of a reference gas (CO_2 with a known $^{13}C/\ ^{12}C$ and H_2 with a known D/H). The standard mix consisting of VOCs with known δD and $\delta^{13}C$ values was used to monitor accuracy and precision of the isotope ratio measurements on a daily basis. The standard deviations (SD) of those analyses were typically less than 5 ‰ for δD (except cumene with 6 ‰) and less than 0.4 ‰ for $\delta^{13}C$.

3.3 Results and Discussion

3.3.1 Variations in Delta Values

The parallel sampling of six TD tubes at each sampling volume (6.8 L, 39 L and 104 L) gave reliable δ values for the VOCs with average SDs of 0.4 ‰ for $\delta^{13}C$ and 3 ‰ for δD analyses. However, SDs varied for all VOCs obtained across different sampling volumes and different sampling days (for $\delta^{13}C$ between 0.0 – 2.0 ‰ with an average of 0.8 ‰ and for δD between 1 - 21 ‰ with an average of 8 ‰). Potential reasons for the slightly elevated SDs are discussed below. For a better understanding all tubes are TD tubes (containing TenaxTA). TD tubes are referred to as "sampling tubes" have been placed in front of "BT tubes" during the sampling collection.

(a) **Operating errors**. Quality control and the verification of low SD from single sampling volumes allowed the exclusion of random and systematic errors.

(b) **Contamination or inadequate blank correction**. All procedure blanks contained <1.5 % of the sample concentration, except for acetic acid (3.7 %) and were consistent at each sampling volume. Environmental conditions were similar for all sampling events and therefore can be excluded as a reason for variations in the δ values.

(c) **Chemical reactions on TenaxTA**. Chemical reactions of VOCs on TenaxTA cannot be totally ruled out because there are limited studies. However, Rothweiler et al. (1991) did not find any indications of chemical reactions occurring for the compounds adsorbed and oxidation by ozone has been reported to be negligible (Venema et al., 1983). Thus it seems unlikely that any chemical reactions have occurred. Oxidative properties of TenaxTA itself could be excluded for alcohols (Yang and Lo, 1997).

(d) **Inadequate retention**. According to Vitzthum von Eckstaedt et al. (2011a) BT of benzene (37 %) and toluene (7 %) had no significant impact on δ values of standard compounds adsorbed on sampling tubes when using TenaxTA. We

monitored BT occurrence for some VOCs (**Table 3.1**) during sampling despite maintaining safe sampling volumes (SSV) for all compounds as recommended by UK-HSE (1993). However, VOCs without any BT showed also elevated SDs across varying sampling volumes. Thus BT cannot entirely account for the variations in SDs.

(e) **Variation of source composition**. Slight variation in the $\delta^{13}C$ and/or δD of the precursor cannot be excluded. Such variations would be transferred to the δ values of the VOCs analysed and cause elevated SDs. An extended sampling series over a longer time frame can clarify if variations in $\delta^{13}C$ and δD for compounds in the emission persist.

Comparing the results of $\delta^{13}C$ and δD analyses (**Figure 3.2** and **Figure 3.4**) it is obvious that fewer δD values are reported. This is due to an increased concentration required for δD analyses.

Table 3.1: Average $\delta^{13}C$ and δD in ‰ and SDs for the VOCs in the calciner stack emission sampled at 6.8 L, 39 L and 104 L.

	compound	$\delta^{13}C \pm SD$	BT $\delta^{13}C \pm SD$	BT (%)	$\delta D \pm SD$	BT $\delta D \pm SD$	BT (%)
alkane	dodecane	-24.5 *					
	tridecane	-25.5 ± 1.0					
	tetradecane	-26.6 ± 0.0			-72 ± 1		
alkene	3-methylene-heptane	-24.9 ± 0.1	-22.7 *	(35%)	-119 ± 9		
	nonene	-28.2 ± 0.2					
	decene	-26.1 ± 1.2					
	dodecene	-25.2 ± 2.0					
	1-tridecene				-26 *		
	undecene	-30.7 ± 0.7					
aromatic	benzene	-23.2 ± 1.5	-22.9 ± 0.4	(38%)	-7 ± 15	-17 ± 8	(59%)
	toluene	-24.3 ± 0.3	-24.1 ± 0.4	(24%)	30 ± 21	15 ± 10	(23%)
	naphthalene	-22.7 ± 0.8			-11 ± 10		
ketone	methyl venyl ketone				-66 ± 3		
	2-pentanone	-23.3 ± 0.5	-22.8 ± 0.9	(24%)	-70 ± 10	-74 ± 13	(34%)
	2-hexanone	-22.8 ± 0.5			-57 ± 7		
	octanone	-22.1 ± 0.1					
artefact	3-heptanone	-27.5 ± 0.7			-105 ± 1		
	acetophenone	-25.6 ± 1.5	-27.5 *	(59%)	-49 *		
	benzaldehyde	-26.2 ± 1.6	-24.7 *	(41%)			
	benzonitrile	-25.3 ± 0.2					
other	2-ethyl-hexanol	-28.1 ± 0.2	-26.6 ± 0.3	(7%)	-135 ± 9	-125 ± 15	(13%)
	2-ethyl-hexanal	-29.3 ± 1.0					
	hexanoic acid				-66 ± 5		

* single analysis BT…breakthrough

3.3.2 $\delta^{13}C$ of VOCs in Calciner Stack Emission

The $\delta^{13}C$ of VOCs in the calciner industry stack emissions range between -22 to -31 ‰ for compounds including *n*-alkanes (C_{12}-C_{14}), *n*-alkenes (C_8-C_{12}), aromatics (C_6-C_{10}), ketones (C_5-C_8) and *n*-alcohol (C_8) (**Table 3.1**). The median $\delta^{13}C$ values range between -24.5 to -26.6 ‰, -24.9 to -30.7 ‰, -22.7 to -24.3 ‰, -22.1 to -27.5 ‰ and -28.1 ‰, respectively for the latter compound classes.

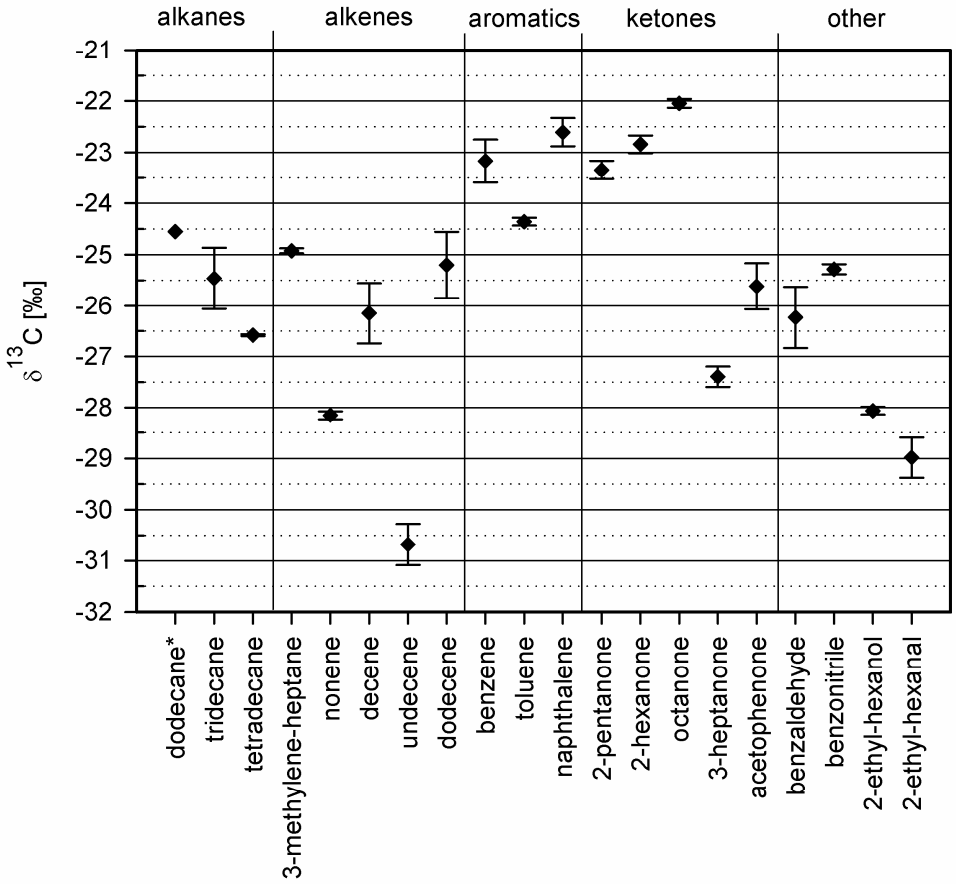

Figure 3.2: Median $\delta^{13}C$ values and error of analyses in ‰ of VOCs in the calciner stack emission (*single analysis).

Some VOCs show different behaviours in their compound class in regards to the $\delta^{13}C$ values (**Figure 3.2**) which indicates a possible source difference; e.g. the δ values for undecene, 3-heptanone and acetophenone are significantly lighter than any other of their group. Interestingly undecene may be a component in the hydrocarbon carrier present in the additives used in the calcination process. After digestion, clarification and precipitation calcination is the fourth step of

the Bayer refining process to turn bauxite into aluminium. Aluminium hydrate crystals are calcined to drive off the molecules of hydrated water by a carefully controlled process. Additives are used in the Bayer process to modify the physical and chemical properties of the final product, e.g. flocculation, dewatering or anti-foaming, etc.. 3-heptanone and acetophenone could also be attributed to the additives but have been previously reported to be artefacts formed on TenaxTA during ozonation, so was benzaldehyde and benzonitrile (Rothweiler et al., 1991; Clausen and Wolkoff, 1997; Lee et al., 2006). However, the amount of these collected compounds and their concentrations with sampling volume are suggested to be a component of the emission and are not formed on TenaxTA after sampling. Ozonation tests in combination with CSIA could clarify their origin. 2-ethylhexanol is a known hydrolysis by-product of the dewatering aid (DWA) to decrease the water content of the hydrate before calcination and is a component always used in the alumina refinery process. 2-ethyl-hexanal is potentially derived from the oxidation of 2-ethyl-hexanol based on their structures. Ozone could be the potential oxidiser due to the presence of ozonation artefacts (see above). The direction of $\delta^{13}C$ differences of 2-ethyl-hexanol and 2-ethyl-hexanal also supports a relation between these compounds. The δ value of 2-ethylhexanal is 1.2 ‰ lighter than the δ value of 2-ethylexanol which would be expected due to the fact that ^{12}C is thermodynamically more favourable during chemical reactions.

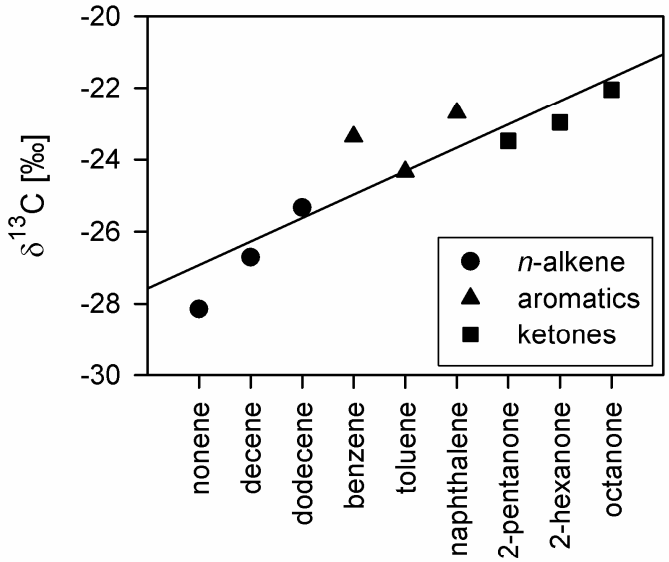

Figure 3.3: Median $\delta^{13}C$ values in ‰ of each compound of each class (i.e. alkenes, aromatics and ketones). The regression line represents the average of the median δ values of VOCs in each class.

The $\delta^{13}C$ relationship between the alkenes, aromatics and ketones as illustrated in **Figure 3.3**is comparable to other natural products (Stahl, 1978; Goni and Eglinton, 1996) where an increasing enrichment in ^{13}C is evident in relatively more polar compounds. This has been attributed to a contribution from lignin and sugars in the more polar fraction of crude oil. Therefore it is suggested that the VOCs in the stack emission reflect a contribution from organic matter containing high amounts of lignin. Given that bauxite is collected in regions with significant wood occurrence (Koch, 2007) the $\delta^{13}C$ values of the relatively more polar VOCs express a greater contribution from lignin.

The average $\delta^{13}C$ value of the analysed VOCs in this study of -25.5 ± 2.5 ‰ (excluding possible artefacts as indicated in **Table 3.1**) confirms results from Turner et al. (2006) and is similar to average $\delta^{13}C$ values derived from car

related emissions reported by others (Rudolph et al., 2002; Turner et al., 2006; Peng et al., 2009). In contrast Giebel et al. (2010) reported significantly lighter $\delta^{13}C$ values for 2-pentanone (-35.2 ‰), benzene (-26.9 ‰) and toluene (-27.5 ‰) collected from a 1972 non-catalytic car. $\delta^{13}C$ values of 2-3 rings aromatic products produced from pyrolysis of coals were reported to be -25.0 ± 0.7 ‰ and diesel at -28.6 ± 0.5 ‰ (McRae et al., 1996).

It is necessary to mention that the method development for TD-GC-irMS on TenaxTA was conducted for aromatic VOCs only. Therefore isotopic fractionation of other compounds analysed in this study cannot be fully excluded, however, it is very unlikely. If isotopic fractionation would have occurred then incomplete desorption from the adsorbent material is assumed to be the main cause. The recovery rate of VOCs adsorbed on TenaxTA was majorly investigated for hydrocarbons together with chlorinated compounds (Kuntasal et al., 2005; Ras et al., 2009). Only a few studies reported recoveries of other compounds like hexanal (97.3+/-6.3) (Rothweiler et al., 1991), octane (94%), undecane (95%) and dodecane (95%)(Kuntasal et al., 2005). Rothweiler et al. (1991) demonstrated that VOCs with a boiling point of up to 270°C could be quantitatively desorbed using Tenax TA. In our study compounds with a boiling point between 60 - 253°C have been investigated. Therefore we believe that TenaxTA is likely to be a suitable adsorbent for all compounds measured in this study.

3.3.3 δD of VOCs in Calciner Stack Emission

For the first time δD values of atmospheric VOC (C_6-C_{10}) are reported (**Figure 3.4**) including i.e. aromatics, ketones, *n*-alkane (-72 ‰) and *n*-alkene with average δD values ranging between -135 to 30 ‰ (see **Table 3.1**). Compared to other natural sources as described in Grice and Brocks (2011) most of the δD results of analysed VOCs are significantly enriched in D. This is possibly attributed in part to isotopic fractionation associated with VOCs condensing in the water phase during emission collection (see section 3.2.4), although no significant quantities of VOCs in the condensed water were detected in a

previous study by Fisher et al. (2003) using GC-MS analysis. On the other hand Wang and Huang (2001, 2003) established depleted δD of liquid toluene, benzene and *n*-alkenes (18.4 ‰, 7.7 ‰ and < 14 ‰), respectively) during progressive evaporation with 80 % loss of liquid. The isotopic fractionation occurs due to intermolecular van der Waals forces present in hydrocarbons where the binding energy decreases with an increasing number of D atoms. Assuming condensation is the direct reverse process to evaporation it is suggested that some isotopic fractionation due to condensation may have occurred during the cooling process. Given that Wang and Huang (2003) reported depletion in D in the remaining liquid of only 18.4 ‰ and 7.7 ‰ for toluene and benzene, respectively the δD values of VOCs in this study remain the most heavy values reported so far. For example Hunkeler et al. (2001) compared δD of benzene from different manufacturers with δD values ranging from −28 ‰ to –97 ‰. Sun et al. (2003) reported δD values of PAH from coal tar, jet fuel and gasoline ranging between -32 and -81 ‰. The δD of analysed *n*-alkane and *n*-alkenes in this present study are also isotopically heavier compared to compounds of other natural sources, i.e. crude oil and sediments (Li et al., 2001; Dawson et al., 2005; Dawson et al., 2007; Grice et al., 2009; Maslen et al., 2009; Nabbefeld et al., 2010). Amongst the group of detected ketones δD of 3-heptanone shows a difference of approximately 40 ‰ compared with other compounds in this class and is consistent with $\delta^{13}C$ results (see section 3.3.2) pointing to different sources. 2-Ethyl-hexanol, derived from the dewatering aid (DWA) additive, was found to be the most depleted compound analysed in these samples.

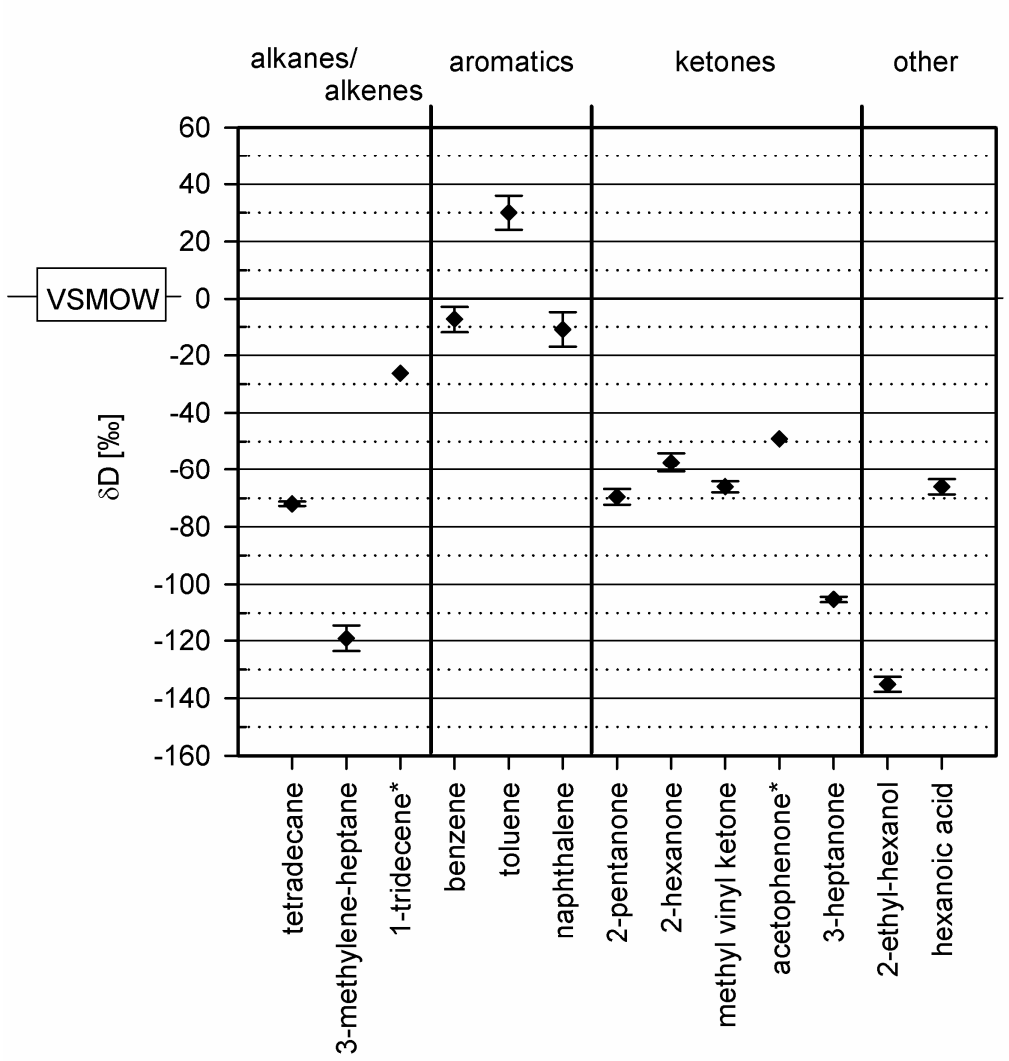

Figure 3.4: Median δD values and error of analyses [‰] of VOCs in the calciner stack emission (*single analysis)

The results obtained in this study show a unique signature for δD of VOCs derived from calcination emission of an alumina refinery. This contains great potential for the ability to track the sources of VOCs in air.

3.4 Conclusions

For the first time a data set was obtained for carbon and hydrogen stable isotope analyses of VOCs in an industry stack emission using solid sorbent sampling with a 6-port sampling train for replicate analysis.

(i) TD-GC-irMS gave reliable results for analysing VOCs with SDs of 0.4 ‰ ($\delta^{13}C$) and 3 ‰ (δD) for single sampling volumes (6.8 L, 39 L and 104 L).

(ii) The slightly elevated SDs across different sampling volumes and different sampling days can be attributed due to possible variations in δ values of the raw organic material whereas BT can have only a minor contribution.

(iii) Average $\delta^{13}C$ values of VOCs in the calcination emission (-24.7 ±1.8 ‰) are similar to other natural sources and reflects their origin (bauxite organics).

(iv) VOCs with depleted $\delta^{13}C$ values are possibly related to additives used in the refinery process

(v) δD results of most VOCs were consistently enriched compared to δD results obtained from other reported natural sources of VOCs. These unusual δD values of atmospheric VOCs are unique and certainly provide a means for tracking VOCs in real atmospheric samples.

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3.5 References

Brass, M., Rockmann, T., 2010. Continuous-flow isotope ratio mass spectrometry method for carbon and hydrogen isotope measurements on atmospheric methane. *Atmospheric Measurement Techniques Discussions* 3, 2433-2476.

Choi, E., Heo, J., Yi, S., 2010. Apportioning and locating nonmethane hydrocarbon sources to a background site in Korea. *Environmental Science & Technology*, 4419-4444.

Clausen, P.A., Wolkoff, P., 1997. Degradation products of Tenax TA formed during sampling and thermal desorption analysis: Indicators of reactive species indoors. *Atmospheric Environment* 31, 715-725.

Clément, M., Arzel, S., Le Bot, B., Seux, R., Millet, M., 2000. Adsorption/thermal desorption-GC/MS for the analysis of pesticides in the atmosphere. *Chemosphere* 40, 49-56.

Coffey, P., Ioppolo-Armanois, M., Cox, S., Jones, M., Logiudice, A., Gwynne, K., 2002. Wagerup refinery air emissions inventory. Alcoa of Australia Limited,

CSIRO, 2004. Wagerup air quality review. The Commonwealth Scientific and Industrial Research Organisation (CSIRO), Aspendale

Dawson, D., Grice, K., Alexander, R., 2005. Effect of maturation on the indigenous δD signatures of individual hydrocarbons in sediments and crude oils from the Perth Basin (Western Australia). *Organic Geochemistry* 36, 95-104.

Dawson, D., Grice, K., Alexander, R., Edwards, D., 2007. The effect of source and maturity on the stable isotopic compositions of individual hydrocarbons in sediments and crude oils from the Vulcan Sub-basin, Timor Sea, Northern Australia. *Organic Geochemistry* 38, 1015-1038.

Fisher, S., 2003. Innovative analytical techniques to differentiate between sources of airborne atmospheric volatile organic compounds (VOCs). 1-18.

Giebel, B., Swart, P., Riemer, D., 2010. $\delta^{13}C$ stable isotope analysis of atmospheric oxygenated volatile organic compounds by gas chromatography-isotope ratio mass spectrometry. *Analytical Chemistry* 82, 6797–6806.

Goldstein, A., Shaw, S., 2003. Isotopes of volatile organic compounds: An emerging approach for studying atmospheric budgets and chemistry. *Chemical Reviews* 103, 5025-5048.

Goni, M.A., Eglinton, T.I., 1996. Stable carbon isotopic analyses of lignin-derived CuO oxidation products by isotope ratio monitoring-gas chromatography-mass spectrometry (irm-GC-MS). *Organic Geochemistry* 24, 601-615.

Grice, K., Brocks, J., 2011. Biomarkers (organic, compound specific isotopes), in: Reitner, J., Thiel, V. (Eds.), Encyclopedia of Geobiology, 1st ed. Springer-Verlag, Berlin, p. 928.

Grice, K., Lu, H., Atahan, P., Asif, M., Hallmann, C., Greenwood, P., Maslen, E., Tulipani, S., Williford, K., Dodson, J., 2009. New insights into the origin of perylene in geological samples. *Geochimica et Cosmochimica Acta* 73, 6531-6543.

Hall, J., Barth, J., Kalin, R., 1999. Routine analysis by high precision gas chromatography mass selective detector isotope ratio mass spectrometry to 0.1 parts per mil. *Rapid Communications in Mass Spectrometry* 13, 1231-1236.

Harrison, R.M., Hester, R.E., 1995. Volatile organic compounds in the atmosphere. *The Royal Society of Chemistry* 1-106.

Hunkeler, D., Anderson, N., Aravena, R., Bernasconi, S., Butler, B., 2001. Hydrogen and carbon isotope fractionation during aerobic biodegradation of benzene. *Environmental Science & Technology* 35, 3462-3467.

Kansal, A., 2009. Sources and reactivity of NMHCs and VOCs in the atmosphere: A review. *Journal of Hazardous Materials* 166, 17-26.

Koch, J., 2007. Restoring a jarrah forest understorey vegetation after bauxite mining in Western Australia. *Restoration Ecology* 15, S26-S39.

Kroupa, A., Dewulf, J., Van Langenhove, H., Víden, I., 2004. Breakthrough characteristics of volatile organic compounds in the -10 to +170° C temperature range on Tenax TA determined by microtrap technology. *Journal of Chromatography A* 1038, 215-223.

Kuntasal, Ö., Karman, D., Wang, D., Tuncel, S., Tuncel, G., 2005. Determination of volatile organic compounds in different microenvironments by multibed adsorption and short-path thermal desorption followed by gas chromatographic–mass spectrometric analysis. *Journal of Chromatography A* 1099, 43-54.

Lee, J., Batterman, S., Jia, C., Chernyak, S., 2006. Ozone artifacts and carbonyl measurements using Tenax GR, Tenax TA, Carbopack B, and Carbopack X adsorbents. *Journal of the Air & Waste Management Association* 56, 1503-1517.

Li, M., Huang, Y., Obermajer, M., Jiang, C., Snowdon, L., Fowler, M., 2001. Hydrogen isotopic compositions of individual alkanes as a new approach to petroleum correlation: case studies from the Western Canada Sedimentary Basin. *Organic Geochemistry* 32, 1387-1399.

Liu, X., Bi, X., Mai, B., Sheng, G., Fu, J., 2005. Separation of PAHs in aerosol by thin layer chromatography for compound-specific stable carbon isotope analysis. *Talanta* 66, 487-494.

Mancini, S.A., Lacrampe-Couloume, G., Sherwood-Lollar, B., 2008. Source differentiation for benzene and chlorobenzene groundwater contamination: A field application of stable carbon and hydrogen isotope analyses. *Environmental Forensics* 9, 177-186.

Maslen, E., Grice, K., Gale, J.D., Hallmann, C., Horsfield, B., 2009. Crocetane: A potential marker of photic zone euxinia in thermally mature sediments and crude oils of Devonian age. *Organic Geochemistry* 40, 1-11.

McRae, C., Love, G.D., Murray, I.P., Snape, C.E., Fallick, A.E., 1996. Potential of gas chromatography isotope ratio mass spectrometry to source polycyclic aromatic hydrocarbon emissions. *Analytical Communications* 33, 331.

Nabbefeld, B., Grice, K., Twitchett…, R., 2010. An integrated biomarker, isotopic and palaeoenvironmental study through the Late Permian event at Lusitaniadalen, Spitsbergen. *Earth and Planetary Science Letter* 291, 84-96.

Nelson, P., Tibbett, A., Day, S., 2008. Effects of vehicle type and fuel quality on real world toxic emissions from diesel vehicles. *Atmospheric Environment* 42, 5291-5303.

O'Sullivan, G., Kalin, R., 2008. Investigation of the range of carbon and hydrogen isotopes within a global set of gasolines. *Environmental Forensics* 9, 166-176.

Okuda, T., Kumata, H., Zakaria, M., Naraoka, H., Ishiwatari, R., Takada, H., 2002. Source identification of Malaysian atmospheric polycyclic aromatic hydrocarbons nearby forest fires using molecular and isotopic compositions. *Atmospheric Environment* 36, 611-618.

Peng, L., Zhang, H., Ren, Z., Mu, L., Shi, R., Chang, L., Li, F., 2009. The carbon isotopic compositions of non-methane hydrocarbons in atmosphere. *Chinese Science Bulletin* 54, 1422-1425.

Philp, R., Allen, J., Kuder, T., 2002. The use of the isotopic composition of individual compounds for correlating spilled oils and refined products in the environment with suspected sources. *Environmental Forensics* 3, 341-348.

Piccot, S., Watson, J., Jones, J., 1992. A global inventory of volatile organic compound emissions from anthropogenic sources. *Journal of Geophysical Research* 97, 9897-9912.

Pilgrim, T.S., Watling, R.J., Grice, K., 2010. Application of trace element and stable isotope signatures to determine the provenance of tea (*Camellia sinensis*) samples. *Food Chemistry* 118, 921-926.

Ras, M., Borrull, F., Marcé, R., 2009. Sampling and preconcentration techniques for determination of volatile organic compounds in air samples. *Trends in Analytical Chemistry* 28, 347-361.

Ribes, A., Carrera, G., Gallego, E., Roca, X., Berenguer, M., Guardino, X., 2007. Development and validation of a method for air-quality and nuisance odors monitoring of volatile organic compounds using multi-sorbent adsorption and gas chromatography/mass spectrometry thermal desorption system. *Journal of Chromatography A* 1140, 44-55.

Rice, A.L., Quay, P.D., 2009. Isotopic composition of formaldehyde in urban air. *Environmental Science & Technology* 43, 8752–8758.

Rothweiler, H., Wäger, P., Schlatter, C., 1991. Comparison of Tenax TA and Carbotrap for sampling and analysis of volatile organic compounds in air. *Atmospheric Environment. Part B. Urban Atmosphere* 25, 231-235.

Rudolph, J., Czuba, E., Norman, A., Huang, L., Ernst, D., 2002. Stable carbon isotope composition of nonmethane hydrocarbons in emissions from transportation related sources and atmospheric observations in an urban atmosphere. *Atmospheric Environment* 36, 1173-1181.

Rudolph, J., Lowe, D., Martin, R., Clarkson, T., 1997. A novel method for compound specific determination of $\delta^{13}C$ in volatile organic compounds at ppt levels in ambient air. *Geophysical Research Letters* 24, 659-662.

Schmidt, T., Zwank, L., Elsner, M., Berg, M., Meckenstock, R., Haderlein, S., 2004. Compound-specific stable isotope analysis of organic contaminants in natural environments: a critical review of the state of the art, prospects, and future challenges. *Analytical and Bioanalytical Chemistry* 378, 283-300.

Slater, G.F., 2003. Stable isotope forensics - When isotopes work. *Environmental Forensics* 4, 13-23.

Stahl, W., 1978. Source rock-crude oil correlation by isotopic type-curves. *Geochimica et Cosmochimica Acta* 42, 1573-1577.

Sun, C., Cooper, M., Snape, C.E., 2003. Use of compound-specific $\delta^{13}C$ and δD stable isotope measurements as an aid in the source apportionment of polyaromatic hydrocarbons. *Rapid Communications in Mass Spectrometry* 17, 2611-2613.

Turner, N., Jones, M., Grice, K., Dawson, D., Ioppolo-Armanios, M., Fisher, S., 2006. $\delta^{13}C$ of volatile organic compounds (VOCs) in airborne samples by thermal desorption-gas chromatography-isotope ratio-mass spectrometry (TD-GC-irMS). *Atmospheric Environment* 40, 3381-3388.

UK-HSE, 1993. MDHS 72 Volatile organic compounds in air. Health and Safety Executive (HSE), United Kingdom

US-EPA, 1999. Determination of volatile organic compounds in ambient air using active sampling onto sorbent tubes (Method TO-17). U.S. Environmental Protection Agency (EPA), Cincinnati, U.S.

US-EPA, 2000. National air pollutant emission trends report, 1900-1998. Office of Air Quality Planning and Standards,

Venema, A., Kampstra, N., Sukkel, J., 1983. Investigation of the possible oxidation by ozone of organic substrates adsorbed on Tenax. *Journal of Chromatography A* 269, 179-182.

Vitzthum von Eckstaedt, C., Grice, K., Ioppolo-Armanios, M., Chidlow, G., Jones, M., 2011. δD and $\delta^{13}C$ analyses of atmospheric volatile organic compounds by thermal desorption gas chromatography isotope ratio mass spectrometry *Journal of Chromatography A* 1218, 6511-6517.

Wang, Y., Huang, Y., 2001. Hydrogen isotope fractionation of low molecular weight *n*-alkanes during progressive vaporization. *Organic Geochemistry* 32, 991-998.

Wang, Y., Huang, Y., 2003. Hydrogen isotopic fractionation of petroleum hydrocarbons during vaporization: implications for assessing artificial and natural remediation of petroleum contamination. *Applied Geochemistry* 18, 1641-1651.

WHO, 2000. Air quality guidelines for Europe. 91, World Health Organization, Copenhagen

Woolfenden, E., 2010. Sorbent-based sampling methods for volatile and semi-volatile organic compounds in air. Part 2. Sorbent selection and other aspects of optimizing air monitoring methods. *Journal of Chromatography A* 1217, 2685-2694.

Yamada, K., Ozaki, Y., Nakagawa, F., Tanaka, M., Yoshida, N., 2003. An improved method for measurement of the hydrogen isotope ratio of atmospheric methane and its application to a Japanese urban atmosphere. *Atmospheric Environment* 37, 1975-1982.

Yang, K.-L., Lo, J., 1997. Evaluation of Tenax-TA adsorption for the measurement of toxic organic compounds in workplace air using thermodesorption/gas chromatography. *Analytical Sciences* 13, 337.

Zalel, A., Yuval, Broday, D.M., 2008. Revealing source signatures in ambient BTEX concentrations. *Environmental Pollution* 156, 553-562.

Zhang, L., Bai, Z., You, Y., Wu, J., Feng, Y., Zhu, T., 2009. Chemical and stable carbon isotopic characterization for PAHs in aerosol emitted from two indoor sources. *Chemosphere* 75, 453-461.

Zielinska, B., Sagebiel, J., Harshfield, G., Gertler, A., Pierson, W., 1996. Volatile organic compounds up to C20 emitted from motor vehicles; measurement methods. *Atmospheric Environment* 30, 2269-2286.

Chapter 4

Compound specific $\delta^{13}C$ and δD analyses of volatile organic compounds in various emissions

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Abstract

This study presents $\delta^{13}C$ and δD values of volatile organic compounds (VOCs) to establish the source of various emissions using thermal desorption-gas chromatography-isotope ratio mass spectrometry (TD-GC-irMS). We found significant differences between δ values of VOCs from a car exhaust, plant combustion experiment (C3 and C4 plants) and industry stack emissions (alumina refinery), e.g. $\delta^{13}C$ of benzene ranged between -21.7 ± 0.2 ‰, -27.6 ± 1.6 ‰, -16.3 ± 2.2 ‰ and -22.5 ± 1.5 ‰, respectively and δD of benzene ranged between -73 ± 13 ‰, -111 ±10 ‰, -70 ± 24 ‰ and -8 ± 15 ‰, respectively. The results of the plant combustion experiment also suggest that the VOCs derived mainly from lignin contributing to the δD values more significantly in dicotyledons than in grasses. δ values of VOCs from petrol car exhaust emissions varied with different tank fuel levels of up to 2 ‰ ($\delta^{13}C$) and up to 25 ‰ (δD). The results of this study indicate that the combination of thermal desorption and compound specific isotope analysis ($\delta^{13}C$ and δD) may be useful for tracing the fate and determining the origin of ambient VOCs in the future.

Keywords

compound specific isotope analysis; industry emission; thermal desorption; biomass combustion; car exhaust emission, source characterization

Brief

Compound specific $\delta^{13}C$ and δD values are established for VOCs from emission sources (car exhaust, biomass combustion, industry stack) using thermal desorption and TenaxTA.

4.1 Introduction

Stable isotope analysis has been used in many studies to differentiate between sources of numerous organic compounds because the isotopic ratios reflect their origin (Schmidt et al., 2004).While bulk stable isotope ratios differ greatly between natural and synthetic products, differences between individual natural sources are often smaller (Philp and Jardé, 2007; Grice and Brocks, 2011). Since different processes and reactions can lead to distinct isotopic signatures due to isotopic fractionations some compound (classes) might be more susceptible and show larger differences than others. Therefore compound specific isotope analysis (CSIA) is an even more powerful tool which increases the potential to differentiate also between various natural materials (Mancini et al., 2008; O'Sullivan and Kalin, 2008). CSIA ($\delta^{13}C$ and δD) originated from geochemical research (Hayes et al., 1990; Schimmelmann et al., 2006) but more recently it has also been applied e.g. to paleoclimate research (e.g. char and ash analysis from plant combustion) (Czimczik et al., 2002; Krull et al., 2003), environmental forensic investigations (Slater, 2003; Pilgrim et al., 2010), and investigations related to degradation pathways and chemical reactions (Elsner et al., 2005; Fischer et al., 2007; Imfeld et al., 2008).

Volatile organic compounds (VOCs) are hydrocarbons (and related compounds) defined by a sufficient vapour pressure to enter the atmosphere under ambient conditions. VOCs are emitted by various anthropogenic (e.g. transportation, industry and biomass burning) and biogenic sources (e.g. microbial production and plant emissions) (Kesselmeier, 1999; Atkinson, 2000; Peñuelas, 2001; Kansal, 2009). However, an anthropogenic source does not necessarily mean a synthetic origin (chemical industry) but also can be derived from natural (e.g. oil, coal, wood) materials. Studying VOCs is very important because they can have an impact on the environment and human health including irritation to disease (WHO, 2000). Their effects have been seen at very low levels of exposure in many epidemiological studies. VOCs are involved in ozone and smog formation and derive from various sources. Investigations of atmospheric components by CSIA can reveal important information about reactions

occurring in the atmosphere. Understanding the fate and tracking the source of a compound can only begin with a detailed knowledge of the source itself.

The literature provides a range of studies investigating $\delta^{13}C$ of VOCs in emissions (Goldstein and Shaw, 2003; Giebel et al., 2010) but only a very few δD values of such compounds in air have been presented to date (Rice and Quay, 2009; Vitzthum von Eckstaedt et al., 2011b; 2011c). Previous research showed that $\delta^{13}C$ alone often could not clearly differentiate between sources of VOCs. For example Turner et al. (2006) showed that the differences between $\delta^{13}C$ values of VOCs in an industry emission compared to those from a car exhaust were negligible. A dual isotope approach (C and H) had effectively distinguished the sources of higher molecular organic compounds like polycyclic aromatic hydrocarbons (PAHs) in a previous study and is therefore anticipated to be a promising tool for establishing sources of VOCs (Sun et al., 2003).

In this study we present, compare and discuss the significance of the $\delta^{13}C$ and δD values of a range of VOCs derived from car exhaust emissions as well as those derived from plant combustion experiments (C3 and C4 plants). The dual approach of $\delta^{13}C$ and δD analyses was used to establish the source of VOCs. For this purpose we applied the recently developed method of thermal desorption-gas chromatography-isotope ratio mass spectrometry (TD-GC-irMS) using TenaxTA as adsorbent material (Vitzthum von Eckstaedt et al., 2011c). A significant distinction was demonstrated between the investigated sources and data from an industry stack emission (alumina refinery).

4.2 Materials and Methods

4.2.1 Sampling Technique

Sampling was conducted in accordance with the method optimised for TD-GC-irMS using stainless steel sampling tubes packed with TenaxTA as described in Vitzthum von Eckstaedt et al. (2011b; 2011c). In brief, the sampling device consisted of six parallel sampling tubes for replicate analyses. The sampling tubes had Silcosteel® coating on the inner wall to protect the sample from

reacting with the metal surface. Sampling volumes varied according to the concentration in the emission. However, the volume flow of 200 ml/min per sampling tube was maintained consistent for all sampling events.

4.2.2 Emission Sources

Two different types of emission sources were sampled:

(i) Car exhaust. Samples were taken from a Ford Laser (year built 1996) running on unleaded petrol (ULP). Samples were taken directly at the exhaust pipe at a high and a low fuel tank level (at 100% and ca. 15%, respectively) from the same fuelling. Sampling with a high fuel tank level (HF) was carried out 14 days prior to sampling the exhaust emission with a low fuel tank level (LF), but samples for $\delta^{13}C$ and δD analyses were taken consecutively on the same day. Prior to sampling the car was run for 20 min and was held at a constant elevated number of revolutions (ca. 3000 rpm) during sampling (steady state). The sampling volume amounted to 4.3 L per sampling tube.

(ii) Plant combustion. A series of plants were chosen according to a difference in their metabolic pathways for carbon fixation in photosynthesis (C3 and C4 plants) (O'Leary, 1988). In total eight different plants were chosen including 5 species of C3 plants and 3 species of C4 plants (**Table 4.1**). The collected plant material (1 kg) contained a representative mix of leaves/needles, bark, duff, twigs and branches (O'Connell and Menage, 1982; Burrows, 1994). The experimental set up included a cylindrical combustion chamber (150 L) with an air blower (to supply an efficient amount of oxygen for oxidation during combustion), a water bath (to reduce the emission temperature in the exhaust pipe) and a 25 m^3 tent (to capture the emitted combustion gases). 2.6 L and 3.0 L samples were taken per sampling tube (C and H analysis, respectively) from inside the tent where ventilators created a homogeneous composition. The combustion temperature was monitored in three zones of the chamber (T_1= above embers, T_2=10 cm above T_1, T_3= at the chamber outlet) and one at the exhaust in the tent (T_4). The maximum temperature occurred during each combustion trial is given in **Table 4.1**. Samples for δD analysis were taken five months prior to samples for $\delta^{13}C$ analysis from separate sampling events. The

amount of 6 parallel samples for each burning experiment revealed SDs for $\delta^{13}C$ analyses between 0 - 1.5 ‰ (average of 0.2 ‰) and for δD analyses between 1 – 11 ‰ (average of 4 ‰).

Table 4.1: Origin of plant species and conditions used to sample VOCs from plant combustion

common plant name	botanical plant name	sampling location	carbon fixation	combustion S_1 [°C]	combustion S_2 [°C]
Jarrah	*Eucalyptus marginata*	SW of WA	C3	906	667
Marri	*Eucalyptus calophylla R.Br.*	SW of WA	C3	1027	952
Karri	*Eucalyptus diversicolor*	SW of WA	C3	908	717
Pine	*Pinus Radiata*	SW of WA	C3	1009	834
Oat	*Avena spp.*	SW of WA	C3	1042	832
Spinifex	*Triodia*	Great Victoria Desert, WA	C4	1009	n.a.
Pilbara Grass	*Themeda triandra*	Hamersley station, WA	C4	791	1090
Kikuyu	*Pennisetum clandestinum*	SW of WA	C4	n.a.	576

SW (south west); WA (Western Australia); S_1 (T_{max} for $\delta^{13}C$ samples); S_2 (T_{max} for δD samples); n.a. (plant material not available)

During the collection of all emissions the ambient temperature was measured at approximately 20 °C and 31 °C (car exhaust and plant combustion sampling, respectively). The sample train was located away from direct sunlight. All TD tubes were transported and stored at 4 °C in an air tight jar containing activated charcoal. Samples were analysed after a maximum of 23 days of storage. According to Vitzthum von Eckstaedt et al. (2011c) this time frame showed a negligible impact on δ values (C, H). The variety of samples of each emission source reflects variations of δ values to give a good representation of the source(s).

4.2.3 TD-GC-MS

Compound identification was determined with a two stage (primary and trap desorption) thermal desorption (TD) unit (Unity2, Markes International Ltd.) linked to a GC-MS (Agilent GC-6890 GC, HP5973 MS detector) operated in scan

range of *m/z* 18-200. The general methodology has been described elsewhere (Bates et al., 2008; Vitzthum von Eckstaedt et al., 2011c). In brief, the GC was equipped with a 60 m x 0.25 mm x 0.25 µm polyethylene glycol column (DB-WAXetr, Agilent J&W) with an initial column flow of 1.1 mL/min. The temperature program was chosen as follows: 5 min isothermal at 35 °C, heated at 5 °C/min to 80 °C, held for 5 min and heated again at 12 °C/min to a final temperature of 240 °C, held for 3 min. The TD transfer line temperature was set at 120 °C. The primary sample desorption was carried out at 300 °C for 5 min with a helium flow of 15 mL/min with either split flow valve closed (for background, transport control and BT tubes) or set >25 mL/min (for sample tubes). The subsequent trap desorption was conducted from 10 °C to 300 °C in 100 °C /min and held for 1 min. The helium flow through the trap was set at 1 mL/min (for background and transport control tubes) or at >25 mL/min (for BT and sample tubes).

4.2.4 TD-GC-irMS

CSIA was performed on a Micromass IsoPrime continuous flow isotope ratio mass spectrometer interfaced with a HP6890 GC, fitted with the same capillary column and programmed with the same temperature settings as for TD-GC–MS analyses. To maintain the same GC column flow as above of 1.1 mL/min at 35 °C the head pressure had to be increased to 140.7 kPa. $\delta^{13}C$ and δD analyses of VOCs in atmospheric samples using TD-GC-irMS were established in a previous study (Vitzthum von Eckstaedt et al., 2011c). In brief, the instrument was routinely checked for linearity, accuracy and precision using an internal standard mix of five compounds (*n*-undecane, *n*- tridecane, *n*-tetradecane, *n*-heptadecane, *n*-octadecane, *n*-nonadecane, pentacosane) with known δD and $\delta^{13}C$ values. During TD-GC-irMS analysis instrument reliability was monitored by using a mix of eleven VOCs (C_6-C_{10}) of known δ values with purities ≥ 99.5 %. Compounds were dissolved in *n*-pentane (2.4 µg/µL, per compound). An aliquot of 2 µL was vaporised in a flow of helium gas using a calibration solution loading rig to introduce the standard mix to a TD tube. Standards were analysed

once a day or after every tenth sample. The standard deviations (SD) of those analyses were less than 0.4 ‰ for $\delta^{13}C$ and typically less than 5 ‰ for δD.

4.3 Results and Discussion

4.3.1 Petrol Car Exhaust Emissions

The emission of a petrol car exhaust was sampled at different times on the same car under similar conditions (ambient temperature, engine parameters), except for the fuel tank level (HF, LF). The results of $\delta^{13}C$ and δD of VOCs ranged between -21.2 to -26.3 ‰ and between -20 to -84 ‰, respectively (**Table 4.2**). The SDs for $\delta^{13}C$ and δD analyses of most individual VOCs are below instrument precision (0.3 ‰ and 5 ‰, respectively) demonstrating consistent δ values for each sampling event. However, comparing the results from HF and LF sampling we observed decreased δD values (up to 19 ‰) for most VOCs in LF samples but an enrichment in D for benzene (25 ‰) and toluene (7 ‰). The cause remains unclear and we suggest to use the presented data as a 'fingerprint' for car related emissions. However, we discuss some possibilities for impacts on the results presented, e.g. equilibrium fractionation between fuel and gas phase in the tank (closed system) cannot account for the monitored δ differences and it is assumed that the tank is isotopically homogeneous. An average fuel emission rate of 0.72 mg/h (model year 1996), observed by Batterman et al. (2005; 2006), can also not cause significant shifts in δD values, for it requires progressive vaporisation of >80 % (Wang and Huang, 2003). Therefore evaporation outside the car can be assumed to be negligable as cause for isotopic fractionation. In modern vehicles, however, fuel pumped from the tank to the engine is subjected to progressive evaporation in the delivery system, where depletion of the liquid phase in heavier isotopes is expect. The returning of the unevaporised fuel will deplete the liquid once it is returned to and mixed with the liquid remaining in the tank and could be the cause for the lighter $\delta^{13}C$ and δD values of VOCs (except benzene and toluene) in the LF samples. Combustion efficiency, e.g. partial burning of the fuel in the engine combustion chamber leads to an increase in NMHC emissions even at steady loads and

speeds (Kayes and Hochgreb, 1999) and might also have an impact on $\delta^{13}C$ and δD values of VOCs in the exhaust emission.

The outcome indicates that δ values of car related emissions can vary significantly and further research is required to investigate which factors determine isotopic fractionation of C and H stable isotopes in car related emissions.

Table 4.2: Average $\delta^{13}C$ and δD values ± SDs (in ‰) of VOCs from car emissions after t=0 (HF[a]) and t=14 d (LF[b]) using the same fuel source.

	$\delta^{13}C$ ± SD					total	δD ± SD					total
compound	**HF**		**LF**		Δ_C	$\delta^{13}C$ ± SD	**HF**		**LF**		Δ_H	δD ± SD
benzene	-21.5 ± 0.2	n=6	-21.8 ± 0.2	n=6	-0.4	-21.7 ± 0.2	-85 ± 3	n=6	-61 ± 3	n=6	25	-73 ± 13
toluene	-22.5 ± 0.2	n=6	-22.6 ± 0.1	n=6	-0.1	-22.6 ± 0.2	-83 ± 1	n=6	-76 ± 1	n=6	7	-80 ± 4
ethylbenzene	-22.7 ± 0.1	n=5	-24.2 ± 0.1	n=5	-1.5	-23.4 ± 0.8	-34 ± 3	n=6	-52 ± 4	n=5	-19	-42 ± 10
p -xylene	-22.4 ± 0.1	n=6	-23.3 ± 0.1	n=6	-1.0	-22.9 ± 0.5	-32		-21 ± 4	n=5		-24 ± 8
m -xylene	-22.9 ± 0.2	n=6	-23.7 ± 0.1	n=6	-0.7	-23.2 ± 0.4	-80 ± 7	n=10	-78 ± 2	n=11	0	-79 ± 5
o -xylene	-22.9 ± 0.1	n=6	-23.2 ± 0.1	n=6	-0.3	-23.1 ± 0.2	-51 ± 5	n=6	-57 ± 3	n=11	-5	-55 ± 5
EMB	-26.3 ± 0.1	n=6		n=6		-26.3 ± 0.1	-30 ± 4	n=7	-48 ± 3	n=7	-19	-39 ± 10
1,2,4-TMB	-23.1 ± 0.1	n=6	-24.0 ± 0.1	n=6	-0.8	-23.6 ± 0.4						
styrene							-40 ± 6	n=5	-46 ± 3	n=2	-5	-42 ± 6
naphthalene	-21.4 ± 0.3	n=6	-23.3 ± 0.0	n=6	-2.0	-22.4 ± 1.0	-73 ± 5	n=5	-79 ± 1	n=5	-6	-76 ± 4

[a] high fuel tank level;

[b] low fuel tank level;

[c] $\delta^{13}C$ difference of LF and HF exhaust emission results;

[d] δD difference of LF and HF exhaust emission results;

EMB – ethyl-methyl-benzene;

TMB – trimethylbenzene;

n=number of analyses

4.3.2 Plant Material Combustion

The investigated plant species included C3 plants such as Jarrah, Karri and Marri (dicotyledons), Pine (conifer) and Oat (grass) as well as C4 plants like Pilbara Grass, Spinifex and Kikuyu (grasses) reflecting their metabolic pathway for CO_2 fixation which causes significant differences in $\delta^{13}C$ values (O'Leary, 1988). Previous syudies reported, e.g. bulk $\delta^{13}C$ values of C3 plant tissue, chars and smoke ranged between −23 and −34% (Turekian et al., 1998; Krull et al., 2003; Das et al., 2010) and bulk C4 plant tissue ranged between −8 and −16% (Das et al., 2010). CSIA for e.g. *n*-alkenes/alkanes and PAHs (Collister et al., 1994; O'Malley et al., 1997) or *n*-alkyl compounds (Pilgrim et al., 2010) showed also a significant difference in $\delta^{13}C$ between plant groups. This study presents CSIA (C, H) results of VOCs emitted from plant combustion with $\delta^{13}C$ values ranging between -23.4 to -30.5 ‰ (C3 plants) and -9.9 to -18.9 ‰ (C4 plants). This trend is consistent with reported literature data (e.g. from ash or plant tissues).

The δD values of VOC from C3 plant combustion emissions range between -55 to -279 ‰ and from C4 plants between -4 to -100 ‰ showing a slight intersection (**Table 4.3**). However, individual VOCs show consistently significantly lighter δD values in C3 plant combustion emissions compared to those from C4 plants, e.g. naphthalene (-96 ‰ and -69 ‰, respectively). The experimental combustion procedures were identical for all plants investigated. The differences in δD values must therefore be related to the raw plant material. Unlike $\delta^{13}C$ the δD values (in leaf water) are rarely affected by the photosynthetic pathway used by plants as found in other studies (Harvey and Welker, 2000; Helliker and Ehleringer, 2002). It is more likely that the δD values are determined by the level of evapotranspiration which is related to leaf morphology. The higher the evapotranspiration rate the heavier the δD values of the leaf water. A study by Smith and colleagues (2006) showed heavier δD values of *n*-alkanes (leaf waxes) in C4 grasses (of about 20 ‰) than in C3 grasses ($\delta D_{C3grass} < \delta D_{C4grass}$). This was attributed to physiology of the plants regulating evapotranspiration rates. C4 plants are characteristically found in

hot, arid environments and show a more efficient use of water, e.g. shorter interveinal distance in the leaves. This is consistent with our δD values of VOCs from C3 grasses (Oats) compared to C4 grasses (Pilbara Gras), e.g. δD of benzene (-122 ‰ and -87 ‰, respectively). But apparently not all findings for *n*-alkanes of leaf waxes can be transferred to VOCs from plant combustion emissions. Research by Chikaraishi and Naraoka (2003) revealed more positive δD values of *n*-alkanes from C3 dicotyledons (e.g. trees) compared to δD of *n*-alkanes from C4 grasses ($\delta D_{C3dicots} > \delta D_{C4grass}$). As concluded by Larcher (2003) this was due to the adaptation of grasses to semi-arid conditions leading to a lower evapotranspiration rate compared to dicotyledons. The δD values of VOCs in our study show an opposite trend ($\delta D_{C3dicots} < \delta D_{C4grass}$). This could indicate that the leaf waxes are not the main source for the VOCs formed during combustion. The generation of aromatic hydrocarbons during combustions has been widely discussed (Richter and Howard, 2000; Lima et al., 2005) but is still not fully understood. Our results suggest that aromatic compounds found in combustion emission from C3 dicotyledons are predominantly derived from lignin/ cellulose which is available in much higher proportions in wood than in grasses (Jaraula et al., 2010). In favour of this hypothesis are the similar δD values of VOC from C3 gymnosperms (e.g. Pine) to C3 angiosperms (e.g. Jarrah) whereas Chikaraishi and Naraoka (2003) found differences between these plant groups in δD of *n*-alkanes (waxes) which was related to isotopic fractionations during lipid synthesis from leaf water.

Table 4.1 shows in the highest temperature reached during the biomass burning experiments which differ in between plants by up to 514 °C. This might reflect real burning incidences where combustion temperature can vary as well. The impact of the combustion temperature on isotope ratios in conjunction with detailed investigations of differences between δD values of plant materials and the link to combustion emission and the ash are currently underway.

Table 4.3: Average δ values for VOCs from C3-plants (5 species) and C4 plants (2 species). Samples taken at t=0 (δD) and t=5 month ($\delta^{13}C$)

	average $\delta^{13}C$ ± SD [‰]			average δD ± SD [‰]		
compounds	**C3 - plants**	**C4 - plants**	**Δ_C**	**C3 - plants**	**C4 - plants**	**Δ_H**
benzene	-27.6 ± 1.6	-16.3 ± 2.2	-11.4	-111 ± 10	-70 ± 24	-41
toluene	-27.1 ± 1.3	-16.0 ± 2.8	-11.1	-81 ± 15	-39 ± 13	-41
ethylbenzene	-26.9 ± 0.8	n.a.		-68 ± 11	n.a.	
m-xylene	-26.3 ± 0.8	n.a.		-138 ± 47	-4	
limonene	-28.2	n.a.		-192 ± 70	n.a.	
eucalyptol	-29.4	n.a.		-248 ± 44	n.a.	
styrene	-26.3 ± 1.5	-14.8 ± 2.2	-11.5	-101 ± 10	-74 ± 25	-27
2-isopropyltoluene	-26.3	n.a.		n.a.	n.a.	
phenylethyne	-26.9	-14.8 ± 2.5	-12.1	n.a.	n.a.	
furfural	-24.7	-11.1 ± 1.7	-13.6	n.a.	-100	
pyrrole	n.a.	n.a.		n.a.	-32	
indene	-27.6 ± 1.6	-17.5 ± 1.9	-10.0	n.a.	n.a.	
benzofuran	-23.7 ± 0.4	n.a.		n.a.	n.a.	
benzaldehyde	-26.4 ± 0.7	n.a.		-172 ± 17	n.a.	
naphthalene	-25.3 ± 0.7	-17.8 ± 0.7	-7.5	-96 ± 10	-69 ± 3	-27

n.a. – data not available (see **Table 4.4** for details)

Table 4.4 lists all compounds analysed for CSIA. Limonene and eucalyptol (1,8-cineole) are monoterpenes and were found in our study only in Eucalyptus (Jarrah, Marri and Karri) and Pine combustion samples. Previous studies investigated a large number of different Australian eucalyptus species and found limonene and eucalyptol in concentrations of 1.0 - 5.1% and 39.3 - 71.7%, respectively in leafs related to the oils in the trees (He et al., 2000; Dunlop et al., 2003). The very light δD values of -242 ‰ and -143 ‰ (limonene) and -279 ‰ and -218 ‰ (eucalyptol) suggesting a biosynthetic pathway relation. Volatilisation is most likely the mechanism for the introduction of these compounds into the smoke plume rather than oxidative combustion (Simoneit et al., 1993). If the light δD is indicative of a biosynthetic origin then benzaldehyde (-184 ‰, -152 ‰ and -181 ‰) is probably also not a combustion product.

Table 4.4: $\delta^{13}C$ and δD of VOCs (‰) of various C3 plant combustion emissions, samples taken at t=0 (δD) and t=5 month ($\delta^{13}C$), n=5

	$\delta^{13}C$ and δD values of C3 - plants										$\delta^{13}C$ and δD values of C4 - plants			
	Jarrah		Karri [2]		Marri		Oat		Pine		Pilbara Grass		Spinifex	Kikuyu
compounds	$\delta^{13}C \pm$ S.D.	$\delta D \pm$ S.D.	$\delta^{13}C \pm$ S.D.	$\delta D \pm$ S.D.	$\delta^{13}C \pm$ S.D.	$\delta D \pm$ S.D.	$\delta^{13}C \pm$ S.D.	$\delta D \pm$ S.D.	$\delta^{13}C \pm$ S.D.	$\delta D \pm$ S.D.	$\delta^{13}C \pm$ S.D.	$\delta D \pm$ S.D.	$\delta^{13}C \pm$ S.D.	$\delta D \pm$ S.D.
benzene	-26.4 ± 0.1	-107 ± 10	-27.3 ± 0.1	-121 ± 5	-26.8 ± 0.1	-98 ± 1	-30.5 ± 0.1	-122 ± 1	-27.1 ± 0.1	-106 ± 3	-14.7 ± 0.1	-87 ± 2	-17.8 ± 0.1	-53 ± 5
toluene	-26.5 ± 0.1	-65 [1]	-26.3 ± 0.2	-102 ± 6	-26.7 ± 0.1	-66 ± 9	-29.4 ± 0.1	-85 ± 1	-26.6 ± 0.1	-86 ± 5	-14.0 ± 0.1	-49 ± 2	-18.0 ± 0.1	-30 [1]
ethylbenzene	[3]	-55 ± 3	-27.5 ± 0.0	[4]	[4]	[4]	[4]	-77 [1]	-26.3 ± 0.0	-70 [1]	[4]	[4]	[4]	[3]
m-xylene	[3]	-121 ± 1	-25.3 ± 0.0	-191 ± 5	-26.7 ± 0.4	[4]	[4]	[4]	-26.8 ± 0.1	-102 [1]	[4]	[4]	[4]	-4 ± 2
limonene	[3]	[3]	-28.2 ± 0.2	-242 ± 2	[3]	-143 ± 2	n.d.	n.d.	[4]	[4]	n.d.	n.d.	n.d.	n.d.
eucalyptol	[4]	[4]	-29.4 ± 0.0	-279 ± 5	[3]	-218 ± 1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
styrene	-25.3 ± 0.4	-89 ± 1	-25.6 ± 0.2	-113 ± 2	-26.0 ± 0.3	-95 ± 1	-29.0 ± 0.1	-108 [1]	-25.4 ± 0.1	-101 ± 4	-13.2 ± 0.0	-91 ± 11	-16.4 ± 0.2	-56 ± 5
phenylethyne	n.d.	n.d.	[3]	[3]	[3]	[4]	[3]	[3]	-26.9 ± 0.2	[3]	-13.0 ± 0.2	[3]	-16.6 ± 0.7	n.d.
furfural	[3]	[3]	[3]	[3]	[3]	[4]	-24.7 ± 1.5	[3]	[4]	[4]	-9.9 ± 0.1	[3]	-12.3 ± 0.1	-100 ± 6
pyrrole	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	[4]	-32 ± 5
indene	[3]	[3]	-27.1 ± 0.5	[3]	-26.6 ± 0.8	[3]	-29.9 ± 0.3	[3]	-26.7 ± 0.1	[4]	-16.2 ± 0.1	[4]	-18.9 ± 0.6	[4]
benzofuran	[4]	[4]	[4]	[4]	-23.9 ± 0.0	[4]	[3]	[3]	-23.4 ± 0.1	[4]	n.d.	n.d.	n.d.	n.d.
benzaldehyde	-25.8 ± 0.3	[3]	[3]	-184 ± 10	-27.2 ± 0.7	-152 ± 2	[3]	[3]	-26.2 ± 0.1	-181 [1]	n.d.	n.d.	[4]	[4]
naphthalene	-24.5 ± 0.3	-83 ± 5	-25.3 ± 0.2	-102 ± 1	-24.8 ± 0.3	-94 ± 3	-26.3 ± 0.4	-109 ± 1	-25.6 ± 0.1	-94 ± 3	-18.3 ± 0.0	-67 ± 7	-17.4 ± 0.1	-71 ± 2

[1] no replicates

[2] δD values have been previously reported elsewhere (Vitzthum von Eckstaedt et al., 2011c)

[3] no baseline separation

[4] insufficient concentration n.d. - not detected

Among the plants investigated pyrrole, a heterocyclic aromatic compound, was only detected in sufficient amounts in Kikuyu emissions showing the most heavy δD value of all measured compounds. Interestingly the combustion temperature for Kikuyu was at 576 °C the lowest of all experiments (**Table 4.1**). Pyrrole can derive from proteins as shown by Britt (2002) where pyrolysed pyroline produced single ringed compounds (pyrrole, benzene, styrene, and benzonitrile) at 700 °C. The crude protein content of Kikuyu is very high (ca 240 g/kg) compared e.g. to the very mature oat (ca 50 g/kg) (Saoub et al., 2005; Fulkerson et al., 2007) and could explain the solely appearance of pyrrole in Kikuyu combustion samples.

4.3.3 Comparison of δ Values of VOCs from Petrol Car Exhaust Emission, Plant Combustion and Industry Stack Emissions

Figure 4.1 shows the results of CSIA (C,H) already described in section 3.1 and 3.2 and the incorporated $\delta^{13}C$ and δD values from the industry emission samples of a calcination process of an alumina refinery in WA, Australia published in a previous study (Vitzthum von Eckstaedt et al., 2011b). Three aromatic compounds - benzene, toluene and naphthalene - were present in all sources used for comparison (**Table 4.2**, **Table 4.4** and **Table 4.5**).

Table 4.5: Average $\delta^{13}C$ and δD values with according SDs of compounds present in an industry stack emission

	alumina refinary [1)]	
compound	$\delta^{13}C \pm SD$	$\delta D \pm SD$
benzene	-23.2 ± 1.5	-7 ± 15
toluene	-24.3 ± 0.3	30 ± 21
naphthalene	-22.7 ± 0.8	-11 ± 10

[1)] δ values are cited from Vitzthum von Eckstaedt et al. (2011b)

Figure 4.1 illustrates the significant differences between VOCs from petrol car exhaust emission, combustion emission of C3 and C4 plants and an industry stack emission obtained by TD-GC-irMS analysis. But the results clearly show that $\delta^{13}C$ or δD analysis by itself cannot effectively discriminate the investigated

sources and that a dual stable isotope approach is crucial for source differentiation of emitted VOCs.

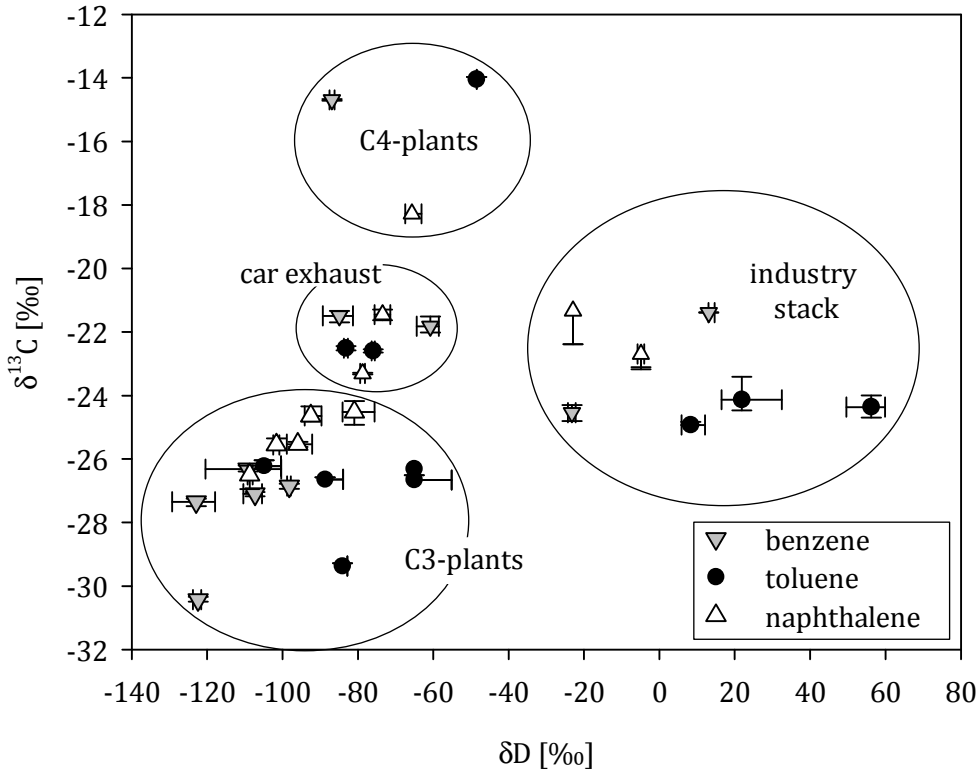

Figure 4.1: Median δ values for benzene, toluene and naphthalene from petrol car exhaust emission (at high and low tank fuel level), C3- and C4 plant combustion emissions (Jarrah, Karri, Marri, Pine, Oat, Pilbara Grass) and industry emissions (at different sampling days and volume). Error bars indicating error of analyses.

4.4 Conclusion

This study could demonstrate the applicability of TD-GC-irMS to various emission sources analysing $\delta^{13}C$ and δD of VOC. Only the combination of $\delta^{13}C$ and δD values allows a successful differentiation between emission categories like car exhaust emission, biomass combustion and industry emissions (alumina refinery).

Results from plant combustion experiments showed that δD values of individual VOCs from C3 dicotyledons are lighter than from C4 grasses. This relation between these plant groups is opposite to results from δD values of compounds in leaf waxes

presented in previous publications. This could indicate that aromatic compounds are not related to the leaf waxes but derive predominantly from lignin/ cellulose.

Samples of car exhaust emissions taken on the same car with the same fuel but with a time lag of 14 days at regular car operation showed significant variations in $\delta^{13}C$ and δD values which can most likely be related to kinetic isotopic fractionation caused by the car engine. Therefore it is to be assumed that differentiations between car related emissions will be most difficult.

4.5 Outlook

The resulting isotopic signatures are distinct and well worth to pursue in future research on source apportionment of emitted VOCs. However, because our study is based on a relatively small number of emissions generalisation of source differentiability on that basis should yet be used with caution. We suggest to extend the range of emission sources e.g. different car models, other industry fields or bush/ forest fires to substantiate the findings in this thesis. Today TD-GC-irMS can be certainly used for establishing further emission sources and investigating reactions where VOCs are involved. It will be also critical to explore the impact of varying processing conditions on the stable isotopes of VOCs from one emission source. The challenge for source tracking will be without doubt to gain enough sample material for stable isotope analysis especially for δD. Extended research is required for using TD-GC-irMS technique also for ambient concentrations. Improvements in sensitivity of analytical instruments and the technical development in general in last few years will increase the application range for this technique.

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4.7 References

Atkinson, R., 2000. Atmospheric chemistry of VOCs and NOx. *Atmospheric Environment* 34, 2063-2101.

Bates, M., Bruno, P., Caputi, M., Caselli, M., De Gennaro, G., Tutino, M., 2008. Analysis of polycyclic aromatic hydrocarbons (PAHs) in airborne particles by direct sample introduction thermal desorption GC/MS. *Atmospheric Environment* 42, 6144-6151.

Batterman, S., Hatzivasilis, G., Jia, C., 2006. Concentrations and emissions of gasoline and other vapors from residential vehicle garages. *Atmospheric Environment* 40, 1828-1844.

Batterman, S., Yu, Y., Jia, C., Godwin, C., 2005. Non-methane hydrocarbon emissions from vehicle fuel caps. *Atmospheric Environment* 39, 1855-1867.

Britt, P.F., Buchanan, A.C., Owens Jr, C.V., Skeen, J.T., 2002. Formation of nitrogen containing polycyclic aromatic compounds from the CO-pyrolysis of carbohydrates and amino acids. *Abstracts of Papers of the American Chemical Society* 223, U586-U586.

Burrows, N.D., 1994. Experimental development of a fire management model for Jarrah (*Eucalyptus marginata* donn ex Sm.) forest, Department of Forestry. Australian National University, Canberra, ACT, pp. 1-302.

Chikaraishi, Y., Naraoka, H., 2003. Compound-specific δD - $\delta^{13}C$ analyses of *n*-alkanes extracted from terrestrial and aquatic plants. *Phytochemistry* 63, 361-371.

Collister, J., Rieley, G., Stern, B., Eglinton, G., Fry, B., 1994. Compound-specific $\delta^{13}C$ analyses of leaf lipids from plants with differing carbon dioxide metabolisms. *Organic Geochemistry* 21, 619-627.

Czimczik, C., Preston, C., Schmidt, M., Werner, R., Schulze, E., 2002. Effects of charring on mass, organic carbon, and stable carbon isotope composition of wood. *Organic Geochemistry* 33, 1207-1224.

Das, O., Wang, Y., Hsieh, Y.-P., 2010. Chemical and carbon isotopic characteristics of ash and smoke derived from burning of C3 and C4 grasses. *Organic Geochemistry* 41, 263-269.

Dunlop, P.J., Bignell, C.M., Hibbert, D.B., Brooker, M.I.H., 2003. Use of gas chromatograms of the essential leaf oils of the genus *Eucalyptus* for taxonomic purposes: *E. subser.Euglobulares* (Blakely). *Flavour Fragrance Journal* 18, 162-169.

Elsner, M., Zwank, L., Hunkeler, D., 2005. A new concept linking observable stable isotope fractionation to transformation pathways of organic pollutants. *Environmental Science & Technology* 39, 6896-6916.

Fischer, A., Theuerkorn, K., Stelzer, N., Gehre, M., Thullner, M., Richnow, H., 2007. Applicability of stable isotope fractionation analysis for the characterization of benzene biodegradation in a BTEX-contaminated aquifer. *Environmental Science & Technology* 41, 3689-3696.

Fulkerson, W., Neal, J., Clark, C.F., Horadagoda, A., Nandra, K.S., Barchia, I., 2007. Nutritive value of forage species grown in the warm temperate climate of Australia for dairy cows: Herbs and grain crops. *Livestock Science* 107, 253-264.

Giebel, B., Swart, P., Riemer, D., 2010. $\delta^{13}C$ stable isotope analysis of atmospheric oxygenated volatile organic compounds by gas chromatography-isotope ratio mass spectrometry. *Analytical Chemistry* 82, 6797–6806.

Goldstein, A., Shaw, S., 2003. Isotopes of volatile organic compounds: An emerging approach for studying atmospheric budgets and chemistry. *Chemical Reviews* 103, 5025-5048.

Grice, K., Brocks, J., 2011. Biomarkers (organic, compound specific isotopes), in: Reitner, J., Thiel, V. (Eds.), Encyclopedia of Geobiology, 1st ed. Springer-Verlag, Berlin, p. 928.

Harvey, F., Welker, J., 2000. Stable isotopic composition of precipitation in the semi-arid north-central portion of the US Great Plains. *Journal of Hydrology* 238, 90-109.

Hayes, J., Freeman, K., Popp, B., Hoham, C., 1990. Compound-specific isotopic analyses: A novel tool for reconstruction of ancient biogeochemical processes. *Organic Geochemistry* 16, 1115–1128.

He, C., Murray, F., Lyons, T., 2000. Monoterpene and isoprene emissions from 15 Eucalyptus species in Australia. *Atmospheric Environment* 34, 645-655.

Helliker, B., Ehleringer, J., 2002. Grass blades as tree rings: environmentally induced changes in the oxygen isotope ratio of cellulose along the length of grass blades. *New Phytologist* 155, 417-424.

Imfeld, G., Aragonés, C., Zeiger, S., Vitzthum von Eckstädt, C., Paschke, H., Trabitzsch, R., Weiss, H., Richnow, H., 2008. Tracking in situ biodegradation of 1, 2-dichloroethenes in a model wetland. *Environmental Science & Technology* 42, 7924-7930.

Jaraula, C., Grice, K., Vitzthum von Eckstädt, C., Twitchett, R., Kelly, D., 2010. Stable carbon and hydrogen isotopes of components derived from controlled burning experiments of C3 and C4 plants and their use as environmental proxies for tracking fire history, Australian Organic Geochemistry conference, Canberra.

Kansal, A., 2009. Sources and reactivity of NMHCs and VOCs in the atmosphere: A review. *Journal of Hazardous Materials* 166, 17-26.

Kayes, D., Hochgreb, S., 1999. Mechanisms of particulate matter formation in spark-ignition engines. 1. Effect of engine operating conditions. *Environmental Science & Technology* 33, 3957-3967.

Kesselmeier, J., 1999. Biogenic volatile organic compounds (VOC): an overview on emission, physiology and ecology. *Journal of Atmospheric Chemistry* 33, 23-88.

Krull, E., Skjemstad, J., Graetz, D., Grice, K., Dunning, W., Cook, G., Parr, J., 2003. ^{13}C-depleted charcoal from C_4 grasses and the role of occluded carbon in phytoliths. *Organic Geochemistry* 34, 1337-1352.

Larcher, W., 2003. Physiological Plant Ecology, 4th ed. Springer, Berlin.

Lima, A.L.c.C., Farrington, J.W., Reddy, C.M., 2005. Combustion-derived polycyclic aromatic hydrocarbons in the environment—A review. *Environmental Forensics* 6, 109 — 131.

Mancini, S.A., Lacrampe-Couloume, G., Sherwood-Lollar, B., 2008. Source differentiation for benzene and chlorobenzene groundwater contamination: A field application of stable carbon and hydrogen isotope analyses. *Environmental Forensics* 9, 177-186.

O'Connell, A., Menage, P., 1982. Litter fall and nutrient cycling in karri (*Eucalyptus diversicolor* F. Muell.) forest in relation to stand age. *Australian Journal of Ecology* 7, 49-62.

O'Leary, M., 1988. Carbon isotopes in photosynthesis. *Bioscience* 38, 328-336.

O'Malley, V., Burke, R., Schlotzhauer, W., 1997. Using GC–MS/Combustion/IRMS to determine the $^{13}C/^{12}C$ ratios of individual hydrocarbons produced from the combustion of biomass materials—application to biomass burning. *Organic Geochemistry* 27, 567-581.

O'Sullivan, G., Kalin, R., 2008. Investigation of the range of carbon and hydrogen isotopes within a global set of gasolines. *Environmental Forensics* 9, 166-176.

Peñuelas, J., 2001. The complexity of factors driving volatile organic compound emissions by plants. *Biologia Plantarum* 44, 481-487.

Philp, R.P., Jardé, E., 2007. Chapter 10 - Application of stable isotopes and radioisotopes in environmental forensics, in: Murphy, B.L., Morrison, R.D. (Eds.), Introduction to Environmental Forensics, Second Edition ed. Elsevier Inc, Amsterdam, pp. 455-512.

Pilgrim, T.S., Watling, R.J., Grice, K., 2010. Application of trace element and stable isotope signatures to determine the provenance of tea (*Camellia sinensis*) samples. *Food Chemistry* 118, 921-926.

Rice, A.L., Quay, P.D., 2009. Isotopic composition of formaldehyde in urban air. *Environmental Science & Technology* 43, 8752–8758.

Richter, H., Howard, J., 2000. Formation of polycyclic aromatic hydrocarbons and their growth to soot - a review of chemical reaction pathways. *Progress in Energy and Combustion Science* 26, 565-608.

Saoub, H., Makhadmeh, I., El-Shatnawi, M.K.J., Haddad, N., Aukour, F.J., 2005. Clipping of Avena sterilis under sub-humid Mediterranean condition. *Crop Research* 29, 77-86.

Schimmelmann, A., Sessions, A.L., Mastalerz, M., 2006. Hydrogen isotopic (D/H) composition of organic matter during diagenesis and thermal maturation. *Annual Review of Earth and Planetary Sciences* 34, 501-533.

Schmidt, T., Zwank, L., Elsner, M., Berg, M., Meckenstock, R., Haderlein, S., 2004. Compound-specific stable isotope analysis of organic contaminants in natural environments: a critical review of the state of the art, prospects, and future challenges. *Analytical and Bioanalytical Chemistry* 378, 283-300.

Simoneit, B., Rogge, W., Mazurek, M., 1993. Lignin pyrolysis products, lignans, and resin acids as specific tracers of plant classes in emissions from biomass combustion. *Environmental Science & Technology* 27, 2533-2541.

Slater, G.F., 2003. Stable isotope forensics - When isotopes work. *Environmental Forensics* 4, 13-23.

Smith, F., Freeman, K., 2006. Influence of physiology and climate on δD of leaf wax *n*-alkanes from C_3 and C_4 grasses. *Geochimica et Cosmochimica Acta* 70, 1172-1187.

Sun, C., Cooper, M., Snape, C.E., 2003. Use of compound-specific $\delta^{13}C$ and δD stable isotope measurements as an aid in the source apportionment of polyaromatic hydrocarbons. *Rapid Communications in Mass Spectrometry* 17, 2611-2613.

Turekian, V., Macko, S., Ballentine, D., Swap, R., Garstang, M., 1998. Causes of bulk carbon and nitrogen isotopic fractionations in the products of vegetation burns: laboratory studies. *Chemical Geology* 152, 181-192.

Turner, N., Jones, M., Grice, K., Dawson, D., Ioppolo-Armanios, M., Fisher, S., 2006. $\delta^{13}C$ of volatile organic compounds (VOCs) in airborne samples by thermal desorption-gas chromatography-isotope ratio-mass spectrometry (TD-GC-irMS). *Atmospheric Environment* 40, 3381-3388.

Vitzthum von Eckstaedt, C., Grice, K., Ioppolo-Armanios, M., Jones, M., 2011a. $\delta^{13}C$ and δD of volatile organic compounds in an alumina industry stack emission. *Atmospheric Environment* 45, 5477-5483.

Vitzthum von Eckstaedt, C., Grice, K., Ioppolo-Armanios, M., Jones, M., Chidlow, G., 2011b. δD and $\delta^{13}C$ analyses of atmospheric volatile organic compounds by thermal desorption gas chromatography isotope ratio mass spectrometry. *Journal of Chromatography A* 1218, 6511-6517.

Wang, Y., Huang, Y., 2003. Hydrogen isotopic fractionation of petroleum hydrocarbons during vaporization: implications for assessing artificial and natural remediation of petroleum contamination. *Applied Geochemistry* 18, 1641-1651.

WHO, 2000. Air quality guidelines for Europe. 91, World Health Organization, Copenhagen

Chapter 5

Conclusions

Results are presented in Chapter 2 to establish the reliability of TD-GC-irMS (using TenaxTA as an adsorbent material) for δD and $\delta^{13}C$ analysis of a range of VOCs (C_6 - C_{10}) with standard deviations below instrument precision. A comparison of the δ values to those obtained by GC-irMS (without TD) confirmed negligible isotopic fractionation during TD-GC-irMS. A number of tests proved the robustness of the sampling and analysis procedure of TD-GC-irMS (e.g. storage and impact of BT). The results also demonstrated that samples collected from the split flow effluent during TD could be used for further analysis including isotope analysis. Obtaining a replicate sample saved valuable sampling time and resources. The application of TD-GC-irMS of the same VOCs from three different emission sources demonstrated the power and limitations of TD-GC-irMS. Significant differences were found between δD of VOCs from petrol car exhaust emission compared to emissions from biomass combustions (e.g. a Karri tree). However, the content of a highly complex unresolved mixture in the diesel exhaust emission sample prevented GC baseline separation of VOCs of interest and thus caused elevated standard deviations and less reliable δ values.

Chapter 3 describes the sampling and analysis procedure to obtain δD and $\delta^{13}C$ values of a range of VOCs from an industry stack emission of an alumina refinery. A newly designed sampling train allowed the multiple collection of the required sample material for δD and $\delta^{13}C$ analyses. The analysis of samples adsorbed on TenaxTA showed SDs of 0.4 ‰ ($\delta^{13}C$) and 3 ‰ (δD) for the investigated VOCs. However, δ values of VOCs varied between samples taken on different days with different sampling volumes. These variations were attributed to possible variations in δ values of the raw organic material (organic material in bauxite ore) whereas BT was found to have a secondary effect on the measured δ values. Results obtained from $\delta^{13}C$ analyses showed a similar correlation between various compound classes previously reported for natural sources and is consistent with an origin of the VOCs from organic deposits in bauxite ore. Results obtained from δD analyses were consistently enriched for most VOCs compared to those from other natural sources. These unusual δD

values of atmospheric VOCs are unique and certainly provide a means for tracking VOCs in real atmospheric samples.

Results presented in Chapter 4 demonstrated the application of compound specific isotope analysis of two elements, e.g. δD and $\delta^{13}C$ of VOCs in a number of emission samples. VOCs were sampled from car exhaust emissions (petrol engine); emissions from biomass combustions (C3 and C4 plants) and emissions from an industry stack (alumina refinery). The comparison of the δ values of VOCs occurring in all investigated emissions sources showed significant differences reflecting the origin of the compounds. The statistical analysis of most VOCs across all emission sources investigated showed standard deviations below instrument precision and thus confirmed the reliability of TD-GC-irMS to establish sources of VOCs in the different emissions. The δ results obtained from the plant combustion experiment indicated that VOCs were derived mainly from lignin/ cellulose which is present in much higher proportions in wood than in grasses. δ values of VOCs from petrol car exhaust emissions varied with different tank fuel levels. The δD values of VOCs from industry stack emission showed distinct differences to the other investigated sources. Despite the variations in all emission sources VOCs can be allocated to their sources when using a combination of compound specific $\delta^{13}C$ and δD analyses.

The results of this PhD study indicate that the combination of active solid sampling on TenaxTA and TD is a suitable technique to introduce atmospheric VOCs into a GC-irMS instrument. TD-GC-irMS has proven to be a valuable method for measuring $\delta^{13}C$ and δD of individual VOCs from various emission sources and can be used for establishing further source(s) in the environment. This capability is may be useful for determining the origin of ambient VOCs in the future and/or can assist in tracking the fate of atmospheric VOCs.

Bibliography

A

Aragón, P., Atienza, J., Climent, M., 2000. Analysis of organic compounds in air: A review. *Critical Reviews in Analytical Chemistry.* 30, 121-151.

Atkinson, R., 2000. Atmospheric chemistry of VOCs and NO_x. *Atmospheric Environment*. 34, 2063-2101

B

Baek, S., Field, R., Goldstone, M., Kirk, P., Lester, J., Perry, R., 1991. A review of atmospheric polycyclic aromatic hydrocarbons: sources, fate and behavior. *Water, Air, and Soil Pollution.* 60, 279-300.

Ballentine, D., Macko, S., Turekian, V., Gilhooly, W., Martincigh, B., 1996. Compound specific isotope analysis of fatty acids and polycyclic aromatic hydrocarbons in aerosols: implications for biomass burning. *Organic Geochemistry.* 25, 97-104.

Bates, M., Bruno, P., Caputi, M., Caselli, M., De Gennaro, G., Tutino, M., 2008. Analysis of polycyclic aromatic hydrocarbons (PAHs) in airborne particles by direct sample introduction thermal desorption GC/MS. *Atmospheric Environment.* 42, 6144-6151.

Batterman, S., Hatzivasilis, G., Jia, C., 2006. Concentrations and emissions of gasoline and other vapors from residential vehicle garages. *Atmospheric Environment* 40, 1828-1844.

Batterman, S., Yu, Y., Jia, C., Godwin, C., 2005. Non-methane hydrocarbon emissions from vehicle fuel caps. *Atmospheric Environment.* 39, 1855-1867.

Brass, M., Rockmann, T., 2010. Continuous-flow isotope ratio mass spectrometry method for carbon and hydrogen isotope measurements on atmospheric methane. *Atmospheric Measurement Techniques Discussions* 3, 2433-2476.

Breteler, W., Grice, K., Schouten, S., Kloosterhuis, H.T., Damste, J.S.S., 2002. Stable carbon isotope fractionation in the marine copepod *Temora longicornis*: unexpectedly low $\delta^{13}C$ value of faecal pellets. *Marine Ecology Progress Series.* 240, 195-204.

Britt, P.F., Buchanan, A.C., Owens Jr, C.V., Skeen, J.T., 2002. Formation of nitrogen containing polycyclic aromatic compounds from the CO-pyrolysis of carbohydrates and amino acids. Abstracts of Papers of the American Chemical Society 223, U586-U586.

Burgøyne, T., Hayes, J., 1998. Quantitative production of H_2 by pyrolysis of gas chromatographic effluents. *Analytical Chemistry.* 70, 5136-5141.

Burrows, N.D., 1994. Experimental development of a fire management model for Jarrah (*Eucalyptus marginata* donn ex Sm.) forest, Department of Forestry. Australian National University, Canberra, ACT, pp. 1-302.

C

Chikaraishi, Y., Naraoka, H., 2003. Compound-specific δD - $\delta^{13}C$ analyses of *n*-alkanes extracted from terrestrial and aquatic plants. *Phytochemistry.* 63, 361-371.

Choi, E., Heo, J., Yi, S., 2010. Apportioning and locating nonmethane hydrocarbon sources to a background site in Korea. *Environmental Science & Technology. 44, 5849–5854*.

Clausen, P.A., Wolkoff, P., 1997. Degradation products of TenaxTA formed during sampling and thermal desorption analysis: Indicators of reactive species indoors. *Atmospheric Environment.* 31, 715-725.

Clément, M., Arzel, S., Le Bot, B., Seux, R., Millet, M., 2000. Adsorption/thermal desorption-GC/MS for the analysis of pesticides in the atmosphere. *Chemosphere.* 40, 49-56.

Coffey, P., Ioppolo-Armanois, M., Cox, S., Jones, M., Logiudice, A., Gwynne, K., 2002. Wagerup refinery air emissions inventory. Alcoa of Australia Limited,

Cole, J.A., Bittner, J.D., Longwell, J.P., Howard, J.B., 1984. Formation mechanisms of aromatic compounds in aliphatic flames. *Combustion and Flame.* 56, 51-70.

Collister, J., Rieley, G., Stern, B., Eglinton, G., Fry, B., 1994. Compound-specific $\delta^{13}C$ analyses of leaf lipids from plants with differing carbon dioxide metabolisms. *Organic Geochemistry.* 21, 619-627.

Comes, P., Gonzalez-Flesca, N., Menard, T., Grimalt, J., 1993. Langmuir-derived equations for the prediction of solid adsorbent breakthrough volumes of volatile organic compounds in atmospheric emission effluents. *Analytical Chemistry.* 65, 1048-1053.

Craig, H., 1957. Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analysis of carbon dioxide. *Geochimica et Cosmochimica Acta.* 12, 133-149.

CSIRO, 2004. Wagerup air quality review. The Commonwealth Scientific and Industrial Research Organisation (CSIRO), Aspendale

Czapiewski, K., Czuba, E., Huang, L., Ernst, D., Norman, A., Koppmann, R., Rudolph, J., 2002. Isotopic composition of non-methane hydrocarbons in emissions from biomass burning. *Journal of Atmospheric Chemistry.* 43, 45-60.

Czaplicka, M., Klejnowski, K., 2002. Determination of volatile organic compounds in ambient air comparison of methods. *Journal of Chromatography A.* 976, 369-376.

Czimczik, C., Preston, C., Schmidt, M., Werner, R., Schulze, E., 2002. Effects of charring on mass, organic carbon, and stable carbon isotope composition of wood. *Organic Geochemistry.* 33, 1207-1224.

D

Das, O., Wang, Y., Hsieh, Y.-P., 2010. Chemical and carbon isotopic characteristics of ash and smoke derived from burning of C3 and C4 grasses. *Organic Geochemistry.* 41, 263-269.

Dawson, D., Grice, K., Alexander, R., 2005. Effect of maturation on the indigenous δD signatures of individual hydrocarbons in sediments and crude oils from the Perth Basin (Western Australia). *Organic Geochemistry.* 36, 95-104.

Dawson, D., Grice, K., Alexander, R., Edwards, D., 2007. The effect of source and maturity on the stable isotopic compositions of individual hydrocarbons in sediments and crude oils from the Vulcan Sub-basin, Timor Sea, Northern Australia. *Organic Geochemistry.* 38, 1015-1038.

Dawson, D., Grice, K., Wang, S., Alexander, R., Radke, J., 2004. Stable hydrogen isotopic composition of hydrocarbons in torbanites (Late Carboniferous to Late Permian) deposited under various climatic conditions. *Organic Geochemistry.* 35, 189-197.

de Groot, P.A., 2004. Handbook of Stable Isotope Analytical Techniques. Elsevier Science, Ham, Belgium.

Demeestere, K., Dewulf, J., De Witte, B., Van Langenhove, H., 2007. Sample preparation for the analysis of volatile organic compounds in air and water matrices. *Journal of Chromatography A.* 1153, 130-144.

Dettmer, K., Engewald, W., 2002. Adsorbent materials commonly used in air analysis for adsorptive enrichment and thermal desorption of volatile organic compounds. *Analytical and Bioanalytical Chemistry.* 373, 490-500.

Dettmer, K., Engewald, W., 2003. Ambient air analysis of volatile organic compounds using adsorptive enrichment. *Journal of Chromatography A.* 57, 339-347.

Dunlop, P.J., Bignell, C.M., Hibbert, D.B., Brooker, M.I.H., 2003. Use of gas chromatograms of the essential leaf oils of the genus *Eucalyptus* for taxonomic purposes: *E.* subser. *Euglobulares* (Blakely). Flavour Fragrance Journal 18, 162-169.

E

Elsner, M., Zwank, L., Hunkeler, D., 2005. A new concept linking observable stable isotope fractionation to transformation pathways of organic pollutants. *Environmental Science & Technology* 39, 6896-6916.

European Environment Agency, 2011. Environmental Terminology and Discovery Service (ETDS) http://glossary.eea.europa.eu/terminology/concept_html?term=voc

F

Fischer, A., Theuerkorn, K., Stelzer, N., Gehre, M., Thullner, M., Richnow, H., 2007. Applicability of stable isotope fractionation analysis for the characterization of benzene biodegradation in a BTEX-contaminated aquifer. *Environmental Science & Technology* 41, 3689-3696.

Fisher, S., 2003. Innovative analytical techniques to differentiate between sources of airborne atmospheric volatile organic compounds (VOCs). 1-18.

Fulkerson, W., Neal, J., Clark, C.F., Horadagoda, A., Nandra, K.S., Barchia, I., 2007. Nutritive value of forage species grown in the warm temperate climate of Australia for dairy cows: Herbs and grain crops. *Livestock Science* 107, 253-264.

G

Giebel, B., Swart, P., Riemer, D., 2010. $\delta^{13}C$ stable isotope analysis of atmospheric oxygenated volatile organic compounds by gas chromatography-isotope ratio mass spectrometry. *Analytical Chemistry* 82, 6797–6806.

Goldstein, A., Shaw, S., 2003. Isotopes of volatile organic compounds: An emerging approach for studying atmospheric budgets and chemistry. *Chemical Review.* 103, 5025-5048.

Goni, M.A., Eglinton, T.I., 1996. Stable carbon isotopic analyses of lignin-derived CuO oxidation products by isotope ratio monitoring-gas chromatography-mass spectrometry (irm-GC-MS). *Organic Geochemistry.* 24, 601-615.

Grice, K., Audino, M., Boreham, C., Alexander, R., Kagi, R., 2001. Distributions and stable carbon isotopic compositions of biomarkers in torbanites from different palaeogeographical locations. *Organic Geochemistry.* 32, 1195-1210.

Grice, K., Brocks, J., in press. Biomarkers (organic, compound specific isotopes), in: Encyclopedia of Geobiology. Reitner, J., Thiel, V. (Eds.), Encyclopedia of Geobiology, 1st ed. Springer-Verlag, Berlin.

Grice, K., Lu, H., Atahan, P., Asif, M., Hallmann, C., Greenwood, P., Maslen, E., Tulipani, S., Williford, K., Dodson, J., 2009. New insights into the origin of perylene in geological samples. *Geochimica et Cosmochimica Acta* 73, 6531-6543.

Grice, K., Nabbefeld, B., Maslen, E., 2007. Source and significance of selected polycyclic aromatic hydrocarbons in sediments (Hovea-3 well, Perth Basin, Western Australia) spanning the Permian-Triassic boundary. *Organic Geochemistry.* 38, 1795-1803.

Grice, K., Schouten, S., Peters, K., Sinninghe Damsté, J., 1998. Molecular isotopic characterisation of hydrocarbon biomarkers in Palaeocene–Eocene evaporitic, lacustrine source rocks from the Jianghan Basin, China. *Organic Geochemistry.* 29, 1745-1764.

Grocke, D., 2002. The carbon isotope composition of ancient CO_2 based on higher-plant organic matter. *Philosophical Transactions of the Royal Society of London. Series A: Mathematical, Physical and Engineering Sciences.* 360, 633-658.

H

Haagen-Smit, A.J., Bradley, C.E., Fox, M.M., 1953. Ozone formation in photochemical oxidation of organic substances. *Industrial and Engineering Chemistry.* 45, 2086–2089.

Hall, J., Barth, J., Kalin, R., 1999. Routine analysis by high precision gas chromatography mass selective detector isotope ratio mass spectrometry to 0.1 parts per mil. *Rapid Communications in Mass Spectrometry.* 13, 1231-1236.

Harper, M., 2000. Sorbent trapping of volatile organic compounds from air. *Journal of Chromatography A.* 885, 129-151.

Harrington, R., Poulson, S., Drever, J., Colberg, P., Kelly, E., 1999. Carbon isotope systematics of monoaromatic hydrocarbons: vaporization and adsorption experiments. *Organic Geochemistry* 30, 765-775.

Harrison, R.M., Hester, R.E., 1995. Volatile Organic Compounds in the Atmosphere. The Royal Society of Chemistry. 1-106.

Harvey, F., Welker, J., 2000. Stable isotopic composition of precipitation in the semi-arid north-central portion of the US Great Plains. *Journal of Hydrology.* 238, 90-109.

Harvey, R.G., 1997. Polycyclic aromatic hydrocarbons. Wiley-VCH, Inc., New York.

Hayes, J., Freeman, K., Popp, B., Hoham, C., 1990. Compound-specific isotopic analyses: A novel tool for reconstruction of ancient biogeochemical processes. *Organic Geochemistry.* 16, 1115–1128.

He, C., Murray, F., Lyons, T., 2000. Monoterpene and isoprene emissions from 15 Eucalyptus species in Australia. *Atmospheric Environment* 34, 645-655.

Helliker, B., Ehleringer, J., 2002. Grass blades as tree rings: environmentally induced changes in the oxygen isotope ratio of cellulose along the length of grass blades. *New Phytologist.* 155, 417-424.

Helmig, D., Vierling, L., 1995. Water adsorption capacity of the solid adsorbents Tenax TA, Tenax GR, Carbotrap, Carbotrap C, Carbosieve SIII, and Carboxen 569 and water management techniques for the atmospheric sampling of volatile organic trace gases. *Analytical Chemistry.* 67, 4380-4386.

Hilkert, A., Douthitt, C., Schluter, H., Brand, W., 1999. Isotope ratio monitoring gas chromatography/mass spectrometry of D/H by high temperature conversion isotope ratio mass spectrometry. *Rapid Communications in Mass Spectrometry.* 13.

Hippelein, M., 2004. Background concentrations of individual and total volatile organic compounds in residential indoor air of Schleswig-Holstein, Germany. *Journal of Environmental Monitoring.* 6, 745-752.

HSE, 1993. Volatile organic compounds in air. Method for the determination of hazardous substances. Health and Safety Executive, London, UK

Hunkeler, D., Anderson, N., Aravena, R., Bernasconi, S., Butler, B., 2001. Hydrogen and carbon isotope fractionation during aerobic biodegradation of benzene. *Environmental Science & Technology.* 35, 3462-3467.

I

Iannone, R., Koppmann, R., Rudolph, J., 2007. A technique for atmospheric measurements of stable carbon isotope ratios of isoprene, methacrolein, and methyl vinyl ketone. *Journal of Atmospheric Chemistry.* 58, 181-202.

Imfeld, G., Aragonés, C., Zeiger, S., Vitzthum von Eckstädt, C., Paschke, H., Trabitzsch, R., Weiss, H., Richnow, H., 2008. Tracking in situ biodegradation of 1, 2-dichloroethenes in a model wetland. *Environmental Science & Technology* 42, 7924-7930.

J

Jaraula, C., Grice, K., Vitzthum von Eckstaedt, C., Twitchett, R., Kelly, D., 2010. Stable carbon and hydrogen isotopes of components derived from controlled burning experiments of C3 and C4 plants and their use as environmental proxies for tracking fire history, Australian Organic Geochemistry conference, Canberra.

Jochmann, M., Blessing, M., Haderlein, S., Schmidt, T., 2006. A new approach to determine method detection limits for compound-specific isotope analysis of volatile organic compounds. *Rapid Communications in Mass Spectrometry.* 20, 3639-3648.

K

Kansal, A., 2009. Sources and reactivity of NMHCs and VOCs in the atmosphere: A review. *Journal of Hazardous materials.* 166, 17-26.

Kayes, D., Hochgreb, S., 1999. Mechanisms of particulate matter formation in spark-ignition engines. 1. Effect of engine operating conditions. *Environmental Science & Technology.* 33, 3957-3967.

Kesselmeier, J., 1999. Biogenic volatile organic compounds (VOC): an overview on emission, physiology and ecology. *Journal of Atmospheric Chemistry* 33, 23-88.

Kinnaman, F., Valentine, D., Tyler, S., 2007. Carbon and hydrogen isotope fractionation associated with the aerobic microbial oxidation of methane, ethane, propane and butane. *Geochimica et Cosmochimica Acta.* 71, 271-283.

Klein-Breteler, W., Grice, K., Schouten, S., Kloosterhuis, H.T., Damste, J.S.S., 2002. Stable carbon isotope fractionation in the marine copepod Temora longicornis: unexpectedly low $\delta^{13}C$ value of faecal pellets. *Marine Ecology Progress Series.* 240, 195-204.

Koch, J., 2007. Restoring a jarrah forest understorey vegetation after bauxite mining in Western Australia. *Restoration Ecology.* 15, S26-S39.

Kroupa, A., Dewulf, J., Van Langenhove, H., Víden, I., 2004. Breakthrough characteristics of volatile organic compounds in the -10 to +170° C temperature range on Tenax TA determined by microtrap technology. *Journal of Chromatography A.* 1038, 215-223.

Krull, E., Skjemstad, J., Graetz, D., Grice, K., Dunning, W., Cook, G., Parr, J., 2003. 13C-depleted charcoal from C4 grasses and the role of occluded carbon in phytoliths. *Organic Geochemistry.* 34, 1337-1352.

Kumar, A., Viden, I., 2007. Volatile organic compounds: Sampling methods and their worldwide profile in ambient air. *Environmental Monitoring Assessment.* 131, 301-321.

Kuntasal, Ö., Karman, D., Wang, D., Tuncel, S., Tuncel, G., 2005. Determination of volatile organic compounds in different microenvironments by multibed adsorption and short-path thermal desorption followed by gas chromatographic–mass spectrometric analysis. *Journal of Chromatography A.* 1099, 43-54.

L

Larcher, W., 2003. Physiological Plant Ecology, 4th ed. Springer, Berlin.

Lee, J., Batterman, S., Jia, C., Chernyak, S., 2006. Ozone artifacts and carbonyl measurements using Tenax GR, Tenax TA, Carbopack B, and Carbopack X adsorbents. *Journal of the Air & Waste Management Association.* 56, 1503-1517.

Lewis, T.E., Crockett, A.B., Siegrist, R.L., 1994. Soil sampling and analysis for volatile organic compounds. *Environmental Monitoring and Assessment.* 30, 213-246.

Li, M., Huang, Y., Obermajer, M., Jiang, C., Snowdon, L., Fowler, M., 2001. Hydrogen isotopic compositions of individual alkanes as a new approach to petroleum correlation: case studies from the Western Canada Sedimentary Basin. *Organic Geochemistry.* 32, 1387-1399.

Lima, A.L.c.C., Farrington, J.W., Reddy, C.M., 2005. Combustion-derived polycyclic aromatic hydrocarbons in the environment - A review. *Environmental Forensics.* 6, 109-131.

Liu, X., Bi, X., Mai, B., Sheng, G., Fu, J., 2005. Separation of PAHs in aerosol by thin layer chromatography for compound-specific stable carbon isotope analysis. *Talanta* 66, 487-494.

M

Mancini, S.A., Lacrampe-Couloume, G., Sherwood-Lollar, B., 2008. Source differentiation for benzene and chlorobenzene groundwater contamination: A field application of stable carbon and hydrogen isotope analyses. *Environmental Forensics.* 9, 177-186.

Markes, 2006. Calibration: Preparing and introducing thermal desorption standards using sorbent tubes. Thermal Desorption Technical Support. Markes International Limited Llantrisant, UK

Maslen, E., Grice, K., Gale, J.D., Hallmann, C., Horsfield, B., 2009. Crocetane: A potential marker of photic zone euxinia in thermally mature sediments and crude oils of Devonian age. *Organic Geochemistry* 40, 1-11.

Mastral, A.M., Callen, M.S., 2000. A review on polycyclic aromatic hydrocarbon (PAH) emissions from energy generation. *Environmenal Science and Technology.* 34, 3051-3057.

Matthews, D., Hayes, J., 1978. Isotope-ratio-monitoring gas chromatography-mass spectrometry. *Analytical Chemistry.* 50, 1465-1473.

McRae, C., Snape, C., Sun, C., Fabbri, D., Tartari, D., Trombini, C., Fallick, A., 2000. Use of compound-specific stable isotope analysis to source anthropogenic natural gas-derived polycyclic aromatic hydrocarbons in a lagoon sediment. *Environmental Science & Technology.* 34, 4684-4686.

Meier-Augenstein, W., 1999. Applied gas chromatography coupled to isotope ratio mass spectrometry. *Journal of Chromatography A.* 842, 351-371.

N

Nabbefeld, B., Grice, K., Twitchett…, R., 2010. An integrated biomarker, isotopic and palaeoenvironmental study through the Late Permian event at Lusitaniadalen, Spitsbergen. *Earth and Planetary Science Letter* 291, 84-96.

Nara, H., Nakagawa, F., Yoshida, N., 2005. Development of two-dimensional gas chromatography/isotope ratio mass spectrometry for the stable carbon isotopic analysis of C_2-C_5 non-methane hydrocarbons emitted from biomass burning. *Rapid Communications in Mass Spectrometry.* 20, 241-247.

Neilson, A.H., 1997. PAHs and related compounds: Biology, 1 ed. Springer, New York.

Nelson, P., Tibbett, A., Day, S., 2008. Effects of vehicle type and fuel quality on real world toxic emissions from diesel vehicles. *Atmospheric Environment* 42, 5291-5303.

O

O'Connell, A., 1987. Litter Dynamics in Karri (*Eucalyptus Diversicolor*) Forests of South- Western Australia. *Journal of Ecology.* 75, 781-796.

O'Leary, M., 1988. Carbon isotopes in photosynthesis. *Bioscience.*, 328-336.

O'Malley, V., Burke, R., Schlotzhauer, W., 1997. Using GC–MS/Combustion/IRMS to determine the $^{13}C/^{12}C$ ratios of individual hydrocarbons produced from the combustion of biomass materials - application to biomass burning. *Organic Geochemistry.* 27, 567-581.

O'Sullivan, G., Kalin, R., 2008. Investigation of the range of carbon and hydrogen isotopes within a global set of gasolines. *Environmental Forensics.* 9, 166-176.

P

Peng, C.-Y., Batterman, S., 2000. Performance evaluation of a sorbent tube sampling method using short path thermal desorption for volatile organic compounds. *Journal of Environmental Monitoring.* 2, 313-324.

Peng, L., Zhang, H., Ren, Z., Mu, L., Shi, R., Chang, L., Li, F., 2009. The carbon isotopic compositions of Non-methane Hydrocarbons in atmosphere. *Chinese Science Bulletin.* 54, 1422-1425.

Peñuelas, J., 2001. The complexity of factors driving volatile organic compound emissions by plants. *Biologia Plantarum* 44, 481-487.

Peters, K.E., Walters, C.C., Moldowan, J.M., 2005. The Biomarker Guide, 2nd ed. Cambridge University Press, Cambridge.

Peters, R., Bakkeren, H., 1994. Sorbents in sampling. Stability and breakthrough measurements. *The Analyst.* 119, 71-74.

Philp, R., Allen, J., Kuder, T., 2002. The use of the isotopic composition of individual compounds for correlating spilled oils and refined products in the environment with suspected sources. *Environmental Forensics* 3, 341-348.

Philp, R.P., Jardé, E., 2007. Chapter 10 - Application of stable isotopes and radioisotopes in environmental forensics, in: Introduction to environmental forensics. Murphy, B.L., Morrison, R.D. (Eds.), 2nd ed. Elsevier Inc, Amsterdam, pp. 455-512.

Piccot, S., Watson, J., Jones, J., 1992. A global inventory of volatile organic compound emissions from anthropogenic sources. *Journal of Geophysical Research.* 97, 9897-9912.

Pilgrim, T.S., Watling, R.J., Grice, K., 2010. Application of trace element and stable isotope signatures to determine the provenance of tea (*Camellia sinensis*) samples. *Food Chemistry.* 118, 921-926.

Prosser, S.J., Scrimgeour, C.M., 1995. High-precision determination of $^{2}H/^{1}H$ in H_2 and H_20 by continuous-flow isotope ratio mass spectrometry. *Analytical Chemistry.* 67, 1992-1997.

Pupek, M., Assonov, S., Mühle, J., Rhee, T., Oram, D., Koeppel, C., Slemr, F., Brenninkmeijer, C., 2005. Isotope analysis of hydrocarbons: trapping, recovering and archiving hydrocarbons and halocarbons separated from ambient air. *Rapid Communications in Mass Spectrometry.* 19, 455-460.

R

Ras-Mallorqui, M., Marce-Recasens, R., Borrull-Ballarin, F., 2007. Determination of volatile organic compounds in urban and industrial air from Tarragona by thermal desorption and gas chromatography–mass spectrometry. *Talanta.* 72, 941-950.

Ras, M.R., Borrull, F., Marcé, R.M., 2009. Sampling and preconcentration techniques for determination of volatile organic compounds in air samples. *Trends in Analytical Chemistry.* 28, 347-361.

Redeker, K.R., Davis, S., Kalin, R.M., 2007. Isotope values of atmospheric halocarbons and hydrocarbons from Irish urban, rural, and marine locations. *Journal of Geophysical Research.* 112, D16307.

Ribes, A., Carrera, G., Gallego, E., Roca, X., Berenguer, M., Guardino, X., 2007. Development and validation of a method for air-quality and nuisance odors monitoring of volatile organic compounds using multi-sorbent adsorption and gas chromatography/mass spectrometry thermal desorption system. *Journal of Chromatography A.* 1140, 44-55.

Rice, A.L., Quay, P.D., 2009. Isotopic composition of formaldehyde in urban air. *Environmental Science & Technology.* 43, 8752–8758.

Richter, H., Howard, J., 2000. Formation of polycyclic aromatic hydrocarbons and their growth to soot - a review of chemical reaction pathways. *Progress in Energy and Combustion Science.* 26, 565-608.

Röckmann, T., Álvarez, C., Walter, S., van der Veen, C., Wollny, A., Gunthe, S., Helas, G., Pöschl, U., Keppler, F., Greule, M., 2010. Isotopic composition of H_2 from wood burning: Dependency on combustion efficiency, moisture content, and δD of local precipitation. *Journal of Geophysical Research.* 115, D17308.

Rothweiler, H., Wäger, P., Schlatter, C., 1991. Comparison of Tenax TA and Carbotrap for sampling and analysis of volatile organic compounds in air. *Atmospheric Environment. Part B. Urban Atmosphere.* 25, 231-235.

Rudolph, J., Czuba, E., Norman, A., Huang, L., Ernst, D., 2002. Stable carbon isotope composition of nonmethane hydrocarbons in emissions from transportation related sources and atmospheric observations in an urban atmosphere. *Atmospheric Environment.* 36, 1173-1181.

Rudolph, J., Lowe, D., Martin, R., Clarkson, T., 1997. A novel method for compound specific determination of $\delta^{13}C$ in volatile organic compounds at ppt levels in ambient air. *Geophysical Research Letter.* 24, 659-662.

Rudolph, J., Müller, K., Koppmann, R., 1990. Sampling of organic volatiles in the atmosphere at moderate and low pollution levels. *Analytica Chimica Acta.* 236, 197-211.

S

Saoub, H., Makhadmeh, I., El-Shatnawi, M.K.J., Haddad, N., Aukour, F.J., 2005. Clipping of *Avena sterilis* under sub-humid Mediterranean condition. *Crop Research* 29, 77-86.

Schimmelmann, A., Sessions, A.L., Mastalerz, M., 2006. Hydrogen isotopic (D/H) composition of organic matter during diagenesis and thermal maturation. *Annual Review of Earth and Planetary Sciences.* 34, 501-533.

Schmidt, T., Zwank, L., Elsner, M., Berg, M., Meckenstock, R., Haderlein, S., 2004. Compound-specific stable isotope analysis of organic contaminants in natural environments: a critical review of the state of the art, prospects, and future challenges. *Analytical and Bioanalytical Chemistry.* 378, 283-300.

Schneider, M., Goss, K., 2009. Systematic investigation of the sorption properties of TenaxTA, Chromosorb 106, Porapak N, and Carbopak F. *Analytical Chemistry.* 81, 3017-3021.

Schüth, C., Taubald, H., Bolaño, N., Maciejczyk, K., 2003. Carbon and hydrogen isotope effects during sorption of organic contaminants on carbonaceous materials. *Journal of Contaminant Hydrology* 64, 269-281.

Sessions, A., Burgoyne, T., Hayes, J., 2001. Correction of H_3^+ contributions in hydrogen isotope ratio monitoring mass spectrometry. *Analytical Chemistry.* 73, 192-199.

Sessions, A.L., 2006. Isotope-ratio detection for gas chromatography. *Journal of Separation Science.* 29, 1946-1961.

Siegrist, R.L., 1991. Volatile organic compounds in contaminated soils: the nature and validity of the measurement process. *Journal of Hazardous materials.* 29, 3-15.

Simoneit, B., Rogge, W., Mazurek, M., 1993. Lignin pyrolysis products, lignans, and resin acids as specific tracers of plant classes in emissions from biomass combustion. *Environmental Science & Technology* 27, 2533-2541.

Slater, G., Dempster, H., Lollar, B., Ahad, J., 1999. Headspace analysis: a new application for isotopic characterization of dissolved organic contaminants. *Environmental Science & Technology.* 33, 190-194.

Slater, G.F., 2003. Stable isotope forensics - When isotopes work. *Environmental Forensics.* 4, 13-23.

Slater, G.F., Ahad, J.M.E., Sherwood-Lollar, B., Allen-King, R., Sleep, B., 2000. Carbon isotope effects resulting from equilibrium sorption of dissolved VOCs. *Analytical Chemistry* 72, 5669-5672.

Smith, F., Freeman, K., 2006. Influence of physiology and climate on [delta] D of leaf wax n-alkanes from C3 and C4 grasses. *Geochimica et Cosmochimica Acta.* 70, 1172-1187.

Stahl, W., 1978. Source rock-crude oil correlation by isotopic type-curves. *Geochimica et Cosmochimica Acta.* 42, 1573-1577.

Sun, C., Cooper, M., Snape, C.E., 2003. Use of compound-specific $\delta^{13}C$ andδD stable isotope measurements as an aid in the source apportionment of polyaromatic hydrocarbons. *Rapid Communications in Mass Spectrometry.* 17, 2611-2613.

T

Turekian, V., Macko, S., Ballentine, D., Swap, R., Garstang, M., 1998. Causes of bulk carbon and nitrogen isotopic fractionations in the products of vegetation burns: laboratory studies. *Chemical Geology.* 152, 181-192.

Turner, N., Jones, M., Grice, K., Dawson, D., Ioppolo-Armanios, M., Fisher, S., 2006. $\delta^{13}C$ of volatile organic compounds (VOCS) in airborne samples by thermal desorption-gas chromatography-isotope ratio-mass spectrometry (TD-GC-IR-MS). *Atmospheric Environment.* 40, 3381-3388.

U

UK-HSE, 1993. MDHS 72 Volatile organic compounds in air. Laboratory method using pumped solid sorbent tubes, thermal desorption and gas chromatography. Health and Safety Executive (HSE), United Kingdom

Urey, H.C., Lowenstam, H.A., Epstein, S., McKinney, C.R., 1951. Measurement of palaeotemperatures and temperatures of the upper Cretaceous of England, Denmark, and Southeastern United States. *American Association of Petroleum Geologists Bulletin.* 62, 399-416.

US-EPA, 1999. Determination of volatile organic compounds in ambient air using active sampling onto sorbent tubes (Method TO-17). U.S. Environmental Protection Agency (EPA), Cincinnati, U.S.

US-EPA, 2000. National air pollutant emission trends report, 1900-1998. Office of Air Quality Planning and Standards. U.S. Environmental Protection Agency (EPA), Cincinnati, U.S.

US-EPA, 2006. Terms of Environment. U.S. Environmental Protection Agency (EPA), Cincinnati, U.S. http://www.epa.gov/OCEPAterms/vterms.html.

V

Venema, A., Kampstra, N., Sukkel, J., 1983. Investigation of the possible oxidation by ozone of organic substrates adsorbed on Tenax. *Journal of Chromatography A.* 269, 179-182.

Vitzthum von Eckstaedt, C., Grice, K., Ioppolo-Armanios, M., Chidlow, G., Jones, M., 2011a. δD and $\delta^{13}C$ analyses of atmospheric volatile organic compounds by thermal desorption gas chromatography isotope ratio mass spectrometry. *Journal of Chromatography A* 1218, 6511-6517.

Vitzthum von Eckstaedt, C., Grice, K., Ioppolo-Armanios, M., Jones, M., 2011b. $\delta^{13}C$ and δD of volatile organic compounds in an alumina industry stack emission. *Atmospheric Environment* 45, 5477-5483.

W

Wang, Y., Huang, Y., 2001. Hydrogen isotope fractionation of low molecular weight n-alkanes during progressive vaporization. *Organic Geochemistry.* 32, 991-998.

Wang, Y., Huang, Y., 2003. Hydrogen isotopic fractionation of petroleum hydrocarbons during vaporization: implications for assessing artificial and natural remediation of petroleum contamination. *Applied Geochemistry.* 18, 1641-1651.

Werner, R.A., Brand, W.A., 2001. Referencing strategies and techniques in stable isotope ratio analysis. *Rapid Communications in Mass Spectrometry.* 15, 501-519.

WHO, 2000. Air Quality Guidelines for Europe. European Series. 2nd. World Health Organization, Copenhagen

Woolfenden, E., 2010a. Sorbent-based sampling methods for volatile and semi-volatile organic compounds in air. Part 1: Sorbent-based air monitoring options. *Journal of Chromatography A*.

Woolfenden, E., 2010b. Sorbent-based sampling methods for volatile and semi-volatile organic compounds in air. Part 2. Sorbent selection and other aspects of optimizing air monitoring methods. *Journal of Chromatography A.* 1217, 2685-2694.

Y

Yamada, K., Ozaki, Y., Nakagawa, F., Tanaka, M., Yoshida, N., 2003. An improved method for measurement of the hydrogen isotope ratio of atmospheric methane and its application to a Japanese urban atmosphere. *Atmospheric Environment* 37, 1975-1982.

Yang, K.-L., Lo, J., 1997. Evaluation of Tenax-TA adsorption for the measurement of toxic organic compounds in workplace air using thermodesorption/gas chromatography. *Analytical Sciences* 13, 337.

Z

Zalel, A., Yuval, Broday, D.M., 2008. Revealing source signatures in ambient BTEX concentrations. *Environmental Pollution.* 156, 553-562.

Zhang, L., Bai, Z., You, Y., Wu, J., Feng, Y., Zhu, T., 2009. Chemical and stable carbon isotopic characterization for PAHs in aerosol emitted from two indoor sources. *Chemosphere* 75, 453-461.

Zielinska, B., Sagebiel, J., Harshfield, G., Gertler, A., Pierson, W., 1996. Volatile organic compounds up to C20 emitted from motor vehicles; measurement methods. *Atmospheric Environment.* 30, 2269-2286.

Zoccolillo, L., Amendola, L., Cafaro, C., Insogna, S., 2005. Improved analysis of volatile halogenated hydrocarbons in water by purge-and-trap with gas chromatography and mass spectrometric detection. *Journal of Chromatography A.* 1077, 181-187.

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